

# Dispersion of Chloroform in a Saturated Porous Media

by

Mohamed Hubail Ajward

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the  
Requirements for the Degree of

**MASTER OF SCIENCE**

In

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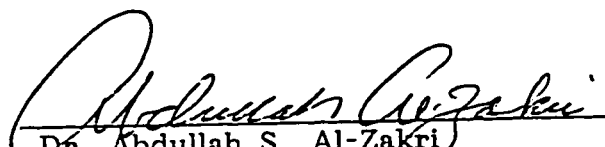
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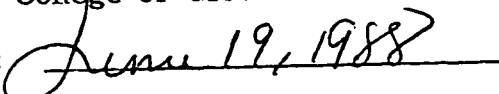
**MOHAMED HUBAIL AJWARD**


under the direction of his thesis committee, and approved by all the members, has been presented to and accepted by the Dean, College of Graduate Studies, in partial fulfillment of the requirements for the degree of

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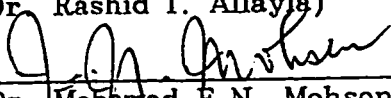
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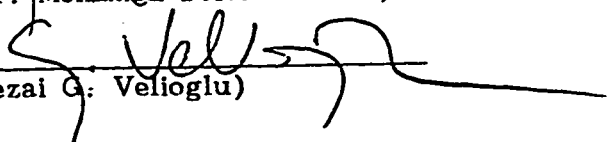
  
Dr. Rashid I. Allayla  
Department Chairman

**Thesis Committee**

  
Chairman (Dr. Achi M. Ishaq)

  
Member (Dr. Rashid I. Allayla)

  
Member (Dr. Mohamed F.N. Mohsen)

  
Member (Sezai G. Velioglu)

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**This Thesis is  
DEDICATED  
to  
MY PARENTS**

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## خلاصة

لقد تم عمل دراسة مخبرية عن امتداد الكلورفورم فى التربة المشبعة المسامية . ولقد تم بناء موديل ترابى فى صندوق من البلكجلاش ، وتتم تجربته بجريان مائى ثابت مع الزمن ومنتظم ، فى التربة المتجانسة المسامية .

هذا وقد تم ادخال مصدر نفطى من محلول الكلورفورم كمصدر ملون . فى التجارب الأولى تم تجريب الكلورفورم كمصدر لحظى . بينما فى التجارب المتأخرة تم حقنه بشكل مستمر . وقد تم أخذ عينات من أماكن متعددة على طول الخطوط المتعامدة على خط الجريان على فترات زمنية . وتم تعيين تراكيز العينات باستعمال جهاز الكروموتغراف .

ولقد تم استخدام النتائج المخبرية فى حل معادلة الانتشار ( الطولى والعرضى ) تحليليا ليتعين معاملات الانتشار الطولى والعرضى للكلورفورم فى التربة المسامية المشبعة وكذلك تم ملاحظة لطور كتلية الكلورفورم وتأثير الاتجاه للصغر مع الزمن . بالإضافة لكل ذلك قد تم تحديد المعامل (  $K_d$  ) للكلورفورم .

\* \* \*

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## ABSTRACT

An experimental investigation into the dispersion of chloroform in a saturated porous media was performed. A plexiglass sand box model was built in the laboratory, and a steady, uniform flow was established in a saturated, homogeneous, isotropic porous media. As a contaminant, a point source of chloroform solution was introduced into the media. In the initial experiments, chloroform solution was introduced as an instantaneous source, while in the latter experiments it was injected as a continuous source. Samples were collected at different locations along and perpendicular to the direction of flow at regular time intervals, and the concentration of the samples were determined using the Gas Chromatograph.

The results of the experiments were used in the analytical solution of the advection-dispersion equation to determine the longitudinal and transverse dispersion coefficients for chloroform in a saturated porous media. Also, the development of the chloroform plume and the attenuation effect was observed. Furthermore, the distribution coefficient  $K_d$  for chloroform was determined.

---

## CHAPTER 1

### 1. INTRODUCTION

In the recent past, concern over the potential migration of wastes in the subsurface has generated a great deal of interest and attention has been focused to the mechanisms responsible for contaminant transport through groundwater systems. Increased attention by both researchers and regulatory agencies to subsurface contamination can be attributed to the growing popularity of waste disposal by means of landfills, sludge lagoons, and deep injection wells [1,2] and to the concern over subsurface disposal of low to high level radioactive wastes [3,4].

Groundwater is a vital natural resource on which many nations are becoming increasingly dependent. In the United States alone, groundwater withdrawals have increased from  $1.3 \times 10^8$  to  $3.3 \times 10^8$  m<sup>3</sup>/day over the last 30 years [5]. Groundwater supplies 25% of the freshwater used for all purposes in the United States, and serves as freshwater for over 95% of the rural population, and approximately one half of all U.S. residents use it as their primary source of drinking water. Current data indicate that in the United States there are at least 17 million waste disposal facilities discharging more than 6.5 billion cubic meters of liquid into the ground each year (U.S. Environmental Protection Agency, 1977).

Reliable and quantitative predictions of contaminant movement can be made only if the processes controlling advection,

hydrodynamic dispersion, and physical, chemical, and biological reactions that affect soluble concentrations in the ground are satisfactorily understood. In the present context, advection refers to movement as a result of differences in head. Dispersion refers to the mixing and spreading caused in part by molecular diffusion and microscopic variations in velocities within individual pores. For many field problems, these effects are negligible in comparison with dispersion caused by large scale heterogeneities within the aquifer. In the presence of large scale heterogeneities, dispersion occurs as contaminants move selectively around the less permeable units. However, when advection is weak, mechanical dispersion is negligible relative to molecular diffusion. Molecular diffusion can be important in low velocity systems, especially where high level radioactive waste is the contaminant.

The major problems associated with contaminant transport in groundwater systems where effects of dispersion are considered to be significant are measuring dispersivity. Moreover, incorporating chemical reactions into these systems is still another difficult problem.

Adsorption of contaminants to soil organic matter is generally proposed to be the primary physicochemical mechanism for altering the fate of such contaminants in saturated groundwater flow. Adsorption is usually incorporated into the advection-dispersion equation in a manner based on the assumption that the concentration of the contaminant in the solution phase is a function of the concentration in the solid phase.

In some situations, the relation between the solution-phase and solid-phase concentrations is linear, and thus the slope of the partitioning function becomes a constant and is generally referred to as the distribution coefficient.

When a source of contaminant enters the saturated zone at the water table, and the contaminant continually flows into the aquifer, a process later referred to as injection, a plume will develop downstream of the source, spreading out to the sides and below. When the aquifer is relatively thin, the vertical extent of the plume is limited by the bottom impermeable boundary. The contaminant quickly mixes over the vertical, and its concentration becomes essentially uniform with depth. When that occurs the plume can be regarded as essentially two dimensional.

In this laboratory study, a steady, uniform flow was established in a saturated, homogeneous, isotropic porous media. As a contaminant, a point source of chloroform solution was introduced into the media. In the initial experiments, chloroform solution was introduced as an instantaneous source, while in the latter experiments it was used as a continuous source, and an attempt was made to determine the longitudinal and transverse dispersion coefficients. Also the development of the plume and its attenuation was observed.

The analytical solution of the advection-dispersion equation is well known [10,33,34,64]. The results of the experiments conducted were used in the analytical solution, and the longitudinal and transverse dispersion coefficients were determined. Furthermore, the

development of the plume trajectory and the plume concentration variation with respect to space and time was studied.

## CHAPTER 2

### 2. LITERATURE REVIEW

#### 2.1 General

Slichter [7], in the course of experiments designed to measure groundwater velocity using salt as a tracer, was among the first to note that dispersion affects the transport of contaminants through a porous medium. Quantitative descriptions of dispersion were attempted in the 1950's by Taylor [8], and Aris [9], among others. Their approach was based on a description of dispersion in capillaries and was reviewed by Bear [10] and by Fried and Combarnous [11] who concluded that it has limited utility for the study of dispersion in porous media.

Statistical models of randomly distributed capillaries were constructed by several researchers including Scheidegger [12], de Josselin de Jong [13], and Saffman [14,15]. This work led to the foundation in the development of the mathematical framework used in the derivation of the macroscopic dispersion equation presented by Bear [10], and others (Bredehoeft et al. [16] and Ogata [17]).

#### 2.2 Conservative Transport

Most knowledge of the dispersion coefficients has been gained through use of experiments on the gross displacement of miscible fluids in porous media.

Rumer [18] obtained longitudinal dispersion coefficients using a

one-dimensional dispersion model in which the average velocity was a constant throughout the length of the flow field. Harleman and Rumer [19] obtained longitudinal and lateral dispersion coefficients by using two, separate, simplified flow experiments. Furthermore, Harleman, Mehlhorn, and Rumer [20] reported on the correlations between the longitudinal dispersion coefficients and the average particle size and the intrinsic permeability.

Along the same line of investigation, Ogata [21,22] included longitudinal and lateral dispersion in his integral solution for the concentration distribution resulting from a step function tracer introduction over a finite area in an axisymmetric flow (one-dimensional seepage); but, he did not consider both longitudinal and lateral dispersion at the same time.

Hoopes and Harleman [23] have given solutions for an instantaneous point-source injection of tracer and for a continuous point-source injection. They solved the advection-dispersion equation for radial steady flow and included the effects of both longitudinal and lateral dispersion. However, they obtained an approximate solution for the radial tracer distribution.

Bruch and Street [24] obtained a theoretical solution for a two dimensional, unsteady dispersion of a miscible second fluid in an idealized, steady, one-dimensional seepage flow through an isotropic porous medium. They derived two simplified mathematical models for determining the dispersion coefficients from a pair of steady-state dispersion experiments. In their study the character and size of the



dispersion pattern was found to be dependent on the contaminant input area, the average seepage velocity, the 50% diameter of the medium, and the kinematic viscosity of the fluid.

Legrand [25] examined the various patterns of contaminated zones in groundwater flow systems and the factors that influence the development and stability of the zones from a qualitative point of view. He concluded that the difficulty in predicting the areal extent of a contaminated zone can be attributed to a number of factors, including the great variety of wastes, the variable pattern of waste disposal, the variable behavior of each contaminant in the subsurface environment, the ranges in geologic and hydrologic conditions in space, and the ranges in hydrologic conditions in time.

Matthess [26], and Rovers and Farquhar [27] described the processes by which contaminated groundwater is purified by natural means. These include mechanical filtration, microbial decomposition, chemical precipitation and co-precipitation, dilution, gaseous exchange, and adsorption. The type of contaminant and the hydrogeologic conditions prevalent determine which of these factors are the most effective. A general review of the physical aspects of groundwater contamination has been given by Cherry et al. [28].

### 2.3 Non Conservative Transport

Hunt [29] obtained a steady state solution for the two-dimensional dispersion from a finite line source while considering radioactive decay. Wolanski [30] later extended Hunt's [29] solution to incor-

porate the three dimensional case.

Marino [31] solved the one dimensional dispersion problem with the input concentration varying exponentially with time. Effects of adsorption, or decay were included in the solution.

Shen [32] derived generalized analytical solutions for transient multidimensional dispersion of non conservative substances in a steady uniform seepage. A finite line or plane boundary source was oriented normal to the flow with time dependent input concentrations. Dispersion in the longitudinal, lateral and transverse directions, linear adsorption isotherms and radioactive decay were also considered. The solutions derived were valid for advection-dispersion in a semi-infinite homogeneous isotropic saturated porous medium. He gave a two dimensional example for the case when the concentration of the line source varied exponentially with time.

Hunt [33] presented one, two and three dimensional solutions for instantaneous, continuous, and steady-state point sources of contamination in a uniform flow field. Then the solutions were used to :

- (1) determine how long a continuous source must be in place before steady state conditions are achieved;
- (2) determine the effect of a finite aquifer depth upon solutions for an aquifer of infinite depth;
- (3) calculate maximum concentrations for instantaneous sources under two different sets of conditions; and
- (4) determine the time required for solutions of a point source and a source of finite size to approach each other.

Wilson and Miller [34] presented exact and approximate solutions

for a common groundwater contamination problem. They considered a two dimensional plume and outlined a graphical method that could be used to better visualize the plume and estimate parameters. As a case study they applied, to the study of a plume of Chromium contamination found on Long Island, New York.

Koltz et al. [35] studied the dispersivity and velocity relationship from laboratory and field experiments. Laboratory experiments were carried out in one-dimensional column devices and in three dimensional flow containers. Tests results demonstrated that it is quite possible up to distances of at least 50 m to transfer results of longitudinal dispersion of artificial grain-size distributions to natural grain-size distributions. Moreover, geological interfaces, which in many cases cause an additional hydrodynamic dispersion, generally cannot be simulated easily in laboratory studies.

### 2.3.1 Trace Organic Contaminant Behavior in Groundwater

The movement and fate of organic materials that enter the subsurface environment are governed by advection, dispersion and adsorption. McCarty, Reinhard, and Rittmann [36] reported that adsorption affects the rate of travel of organic material, relative to that of water, through subsurface systems and allows for the accumulation of organic compounds on the subsurface solid media. Moreover, the hydrophobic organic materials are either adsorbed or absorbed by particulate organic material contained within or on the solid medium, and the extent of adsorption appears to be a function

of the fraction of organic carbon within the subsurface matrix. Furthermore, the partitioning of hydrophobic organics between the water phase and the subsurface organic particulates can be estimated from the octanol/water partition coefficient for each organic compound. This was an important finding, since such values are readily available for many organic compounds or can be determined with relative ease in the laboratory.

Roberts, Reinhard, and Valocchi [37] have given an overview of the nature of organic contaminants found in their surveys of groundwater quality. They have also summarized the salient information regarding the properties of such contaminants and their likely behavior in groundwater, and have shown the relationship between the principles of contaminant behavior in groundwater and the principles of contaminant removal in water treatment.

Piver, and Lindstorm [38] studied a simplified estimation technique for organic contaminant transport in groundwater. In this study they used the analytical solution for the one-dimensional advection-dispersion equation for a single solute in a saturated porous medium. Moreover, they incorporated the adsorption onto soil surfaces and a first-order reaction rate kinetics for the degradation to evaluate the suitability of potential sites for burial of organic chemicals.

## 2.4 Research Objectives

The primary objectives of this study are as follows:

- (1) To determine the longitudinal and transverse dispersion coefficients for chloroform in the saturated porous media. To accomplish this, the results of the experimental study are used in the analytical solution of the advection-dispersion equation.
- (2) To study the development of the contaminant plume variation with respect to space and time.
- (3) To determine the distribution coefficient for chloroform.

## **CHAPTER 3**

### **3. MOVEMENT OF CONTAMINANTS IN GROUNDWATER**

#### **3.1 General Introduction to Organic Contamination of Groundwater**

The widespread use of chemical products, coupled with the need for the disposal of large volumes of waste materials, poses a potential for widely distributed groundwater contamination. New instances of groundwater contamination are continually being recognized. Hazardous chemicals, e.g., pesticides, herbicides, and solvents, are used ubiquitously in everyday life. These and a host of other chemicals are in widespread use in urban, industrial and agricultural settings. Whether intentionally disposed, or accidentally spilled, or applied to the ground for agricultural purposes, some of these chemicals can eventually reach the groundwater and contaminate it. Because of the volumes of toxic wastes and because of their stability in groundwater, such contamination can pose a serious threat to public health and environment.

Effective utilization of the subsurface as a repository for wastes depends on information as to how the wastes are transported. Groundwater is the transporting agent, and it is generally agreed that we know a great deal about the flow of liquids through porous media. However, the problem of contaminant transport is somewhat more complex than the problem of flow.

With conservative contaminant transport a physical mixing occurs that is generally referred to as hydrodynamic dispersion.

Dispersion is caused by both microscopic and macroscopic variations in fluid velocity. On the other hand, with non conservative contaminant transport both organic and inorganic chemical reactions may occur. The analysis of the problem of the reactions and their effect on transport are currently approached from two different directions: (1) studies of overall chemical equilibria and (2) transport analyses involving kinetics.

In the equilibrium approach one assumes that the reactions are sufficiently fast that chemical equilibrium generally is quickly achieved. In this approach the details of the transport process are not taken into account specifically. One needs to only apply the constraints of classical equilibrium geochemistry to understand the chemistry of the system. Much of the current work on chemical contamination has been approached from the framework of equilibrium geochemistry. On the other hand, the transport approach relaxes the equilibrium assumptions. The mathematics is much more complex, and one must have some understanding of the kinetics of the reactions of concern.

Spurred by the awareness of potential environmental hazards and the development of sophisticated analytical equipment, studies of the occurrence and behavior of organic compounds in contaminated groundwater have been initiated recently. Many organic compounds are of environmental concerns in part per billion (ppb) or part per trillion (ppt) quantities. Faced with these problems, research has concentrated on the 120 or so organic compounds designed as priority

pollutants by the US Environmental Protection Agency.

The number and quantity of organic chemicals that are produced have increased continuously since World War II. More than 3,000,000 organic compounds are known to exist and more than 40,000 are currently manufactured [39].

### **3.2 Solute Transport Processes**

The solute transport concepts used by groundwater engineers and hydrogeologists are based on a representation of fluid flow in porous media in which all fluid particles move at identical velocities along parallel streamlines through the porous medium. This conceptual model permits us to express solute transport in porous media by exact mathematical methods, i.e. by a partial differential equation based on Fick's law of diffusion.

A homogeneous, isotropic porous medium may be considered to be any soil, geological stratum or porous medium created in the laboratory in which the mean grain size is the same everywhere, and that the permeability of the unit is independent of the direction of measurements.

#### **3.2.1 Advection**

The driving force of solute transport is that due to hydraulic gradients existing within the porous medium and to molecular diffusion. The component of solute movement attributed to the transport by flowing groundwater is known as advection. Ogata [17] assumed



that solute transport can be approximated by Darcy's law in a macroscopic sense. This 'Darcy' flow makes no allowance for variations in the fluid velocity within the pore, which exist due to the drag effects of the pore wall on the fluid, or from pore to pore, due to differences in shape and diameter. Figure 3.1 shows the average pore water velocity,  $\bar{V}$ , as predicted by the Dupuit-Forcheimer relation and the true velocity distribution,  $V_r$ , that exists because of the drag effects. It is because of this difference that a 'refinement', the dispersion process, was included in the theory developed so that the results from this theory are in accordance with the results observed in the experiments by Ogata [17].

### 3.2.2 Dispersion

Dispersion in porous material refers to the spreading of a stream or discrete volume of dye or contaminant as it flows through the subsurface. If a tracer slug is injected instantaneously into a uniform flow field, it disperses in the direction of flow (longitudinally) and transverse to the direction of flow (laterally). There is a greater dispersion in the direction of flow than transverse to the direction of flow. In an idealized picture as shown in Figure 3.2, the initial point becomes an elliptically shaped cloud whose concentration drops off from the center following a Gaussian distribution. The center of the cloud represents the initial point carried solely by advective transport. The cloud itself is the result of dispersion.

Dispersion causes mixing with uncontaminated groundwater, and

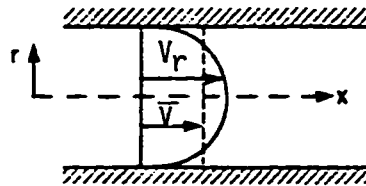


Fig. 3.1. Average Pore Water Velocity,  $\bar{V}$ , as predicted by the Dupuit-Forcheimer relation and the True Velocity Distribution,  $V_r$ , that exists due to drag effects.

Source: Aquifer Contamination and Protection, UNESCO (1980).

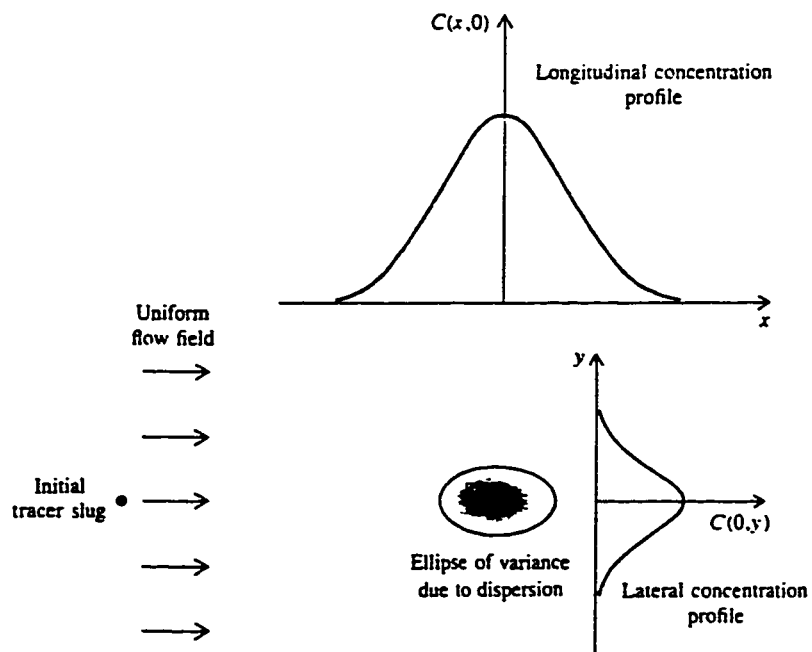


Fig. 3.2. Dispersion of an Instantaneous Point Source in a Uniform Flow Field.

Source: H.F. Wang and M.P. Anderson, Introduction to Groundwater Modeling (1982).

hence dispersion is a mechanism for dilution. Moreover, dispersion causes the contaminant to spread over a greater volume of aquifer than would be predicted solely from an analysis of groundwater velocity vectors. This spreading effect will be of particular concern when toxic or hazardous wastes are involved. Dispersion is chiefly important in predicting transport away from point sources of contamination but is also influential in spreading of nonpoint source contaminations, although of lesser importance. Contaminants introduced into the subsurface from nonpoint sources will be spread over a relatively large area because of the nature of the loading pattern.

Dispersion is of interest because it causes contaminants to arrive at a particular location before the arrival time calculated from the average groundwater velocity,  $\bar{V}$ . The accelerated arrival of contaminants at a particular location is a characteristic feature of dispersion that is due to the fact that some parts of the contaminant plume move faster than the average groundwater velocity,  $\bar{V}$ .

Dispersion is caused by both microscopic and macroscopic effects. Mechanical dispersion on a microscopic scale is a result of deviations of velocity on a microscale from the average groundwater velocity, as shown in Figure 3.3. In addition, it is customary to include molecular diffusion as a component of microscopic dispersion. Molecular diffusion occurs as species move from higher to lower concentrations. Thus, microscopic dispersion includes the effects of mechanical dispersion and molecular diffusion.

On a macroscopic scale, dispersion is caused by the presence

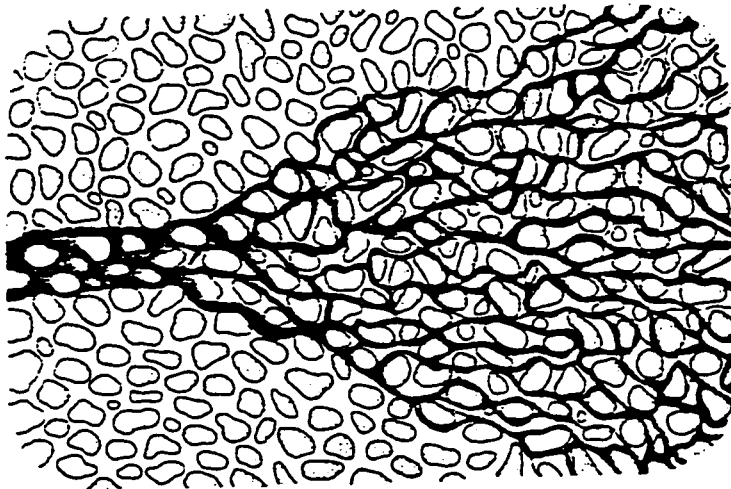


Fig. 3.3. Statistical Distribution of Flow Paths around Local Heterogeneities.  
Source: R.A. Freeze and J.A. Cherry, Groundwater (1979).

of large scale heterogeneities within the subsurface. Skibitzkie and Robinson [40] demonstrated that lenses of high permeability material within a matrix of lower permeability caused the spreading of streams of dye as water and dye moved through a tank filled with sand, as shown in Figure 3.4. It is now generally recognized that the presence of heterogeneities in the subsurface, rather than microscopic dispersion alone, is responsible for the appreciable spreading of contaminants as documented in a number of field studies by Anderson [41].

Pioneering theoretical work on dispersion in air was done by Taylor [8], and serious efforts at applying modified forms of this theory to field studies involving the transport of contaminants in groundwater have been under way since the early 1970's. However, there is still considerable uncertainty concerning methods for quantifying dispersion and for measuring dispersion in the field. To some extent this uncertainty has impeded progress in developing reliable contaminant-transport models. However, within the past 5 years there has been much effort and some progress in quantifying macroscopic dispersion.

The key assumption in deriving a term to represent dispersion is that dispersion can be represented by an expression analogous to Fick's second law of diffusion:

$$\text{Mass flux due to dispersion} = \frac{\partial}{\partial x_i} \left( D_{ij}^* \frac{\partial C}{\partial x_j} \right) \quad (3.1)$$

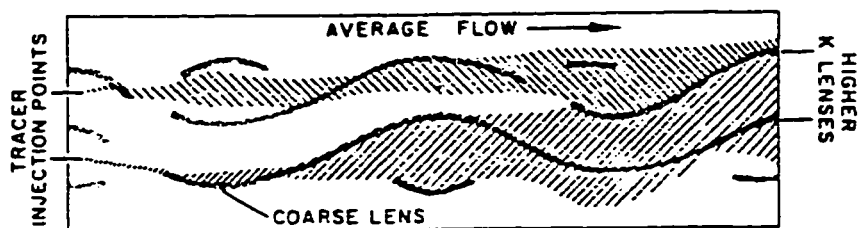


Fig. 3.4. Macroscopic Dispersion.  
Source: Skibitzkie and Robinson, (1963).

where  $C$  is the concentration and  $D_{ij}^*$  is the coefficient of dispersion (the  $i, j$  indices refer to cartesian coordinates). The coefficient of dispersion can be shown to be a second-rank tensor,

$$D_{ij}^* = D_{ij} + D_d \quad (3.2)$$

where  $D_{ij}$  is the coefficient of mechanical dispersion and  $D_d$  is the coefficient of molecular diffusion (a scalar). An effective diffusion coefficient is generally taken to be equal to the diffusion coefficient of the ion in water ( $D_d$ ) times a tortuosity factor. The tortuosity factor has a value less than 1 and is needed to correct for the obstructing effect of the porous medium. Effective diffusion coefficients are generally around  $10^{-6}$  cm<sup>2</sup>/sec, although a range of  $10^{-5}$  to  $10^{-7}$  cm<sup>2</sup>/sec is conceivable (Grisak and Pickens [42]). Except for systems in which groundwater velocities are very low, the coefficient of mechanical dispersion generally will be one or more orders of magnitude larger than  $D_d$ . Therefore, in many practical applications the effects of molecular diffusion may be neglected (i.e.  $D_d = 0$ ).

The coefficient of mechanical dispersion is routinely taken to be the product of the magnitude of the velocity vector times a parameter known as dispersivity, which is commonly and somewhat vaguely referred to as a characteristic mixing length.

Experiments have demonstrated that, in an isotropic medium, the longitudinal and transverse components of dispersion are linearly

dependent on the average velocity of groundwater flow. For a uniform flow field with an average linear velocity equal to  $\bar{V}$

$$D_l = \alpha_l \bar{V} \quad (3.3)$$

and

$$D_s = \alpha_s \bar{V} \quad (3.4)$$

where the parameters  $\alpha_l$  and  $\alpha_s$  are the longitudinal and transverse dispersivities, respectively. The dispersivities are intended to be an intrinsic physical property of the porous medium and have units of length.

Local dispersivities are on the order of  $10^{-2}$  to 1 cm for laboratory experiments and range from  $10^{-1}$  to  $10^2$  m for tracer tests in the more heterogeneous porous material typically encountered in the field [35]. However, it is likely that some of the dispersivities calculated on the basis of field tracer tests are biased by the so-called scale effect as shown in Figure 3.5. Since dispersivity increases with distance from the injection point, some of the values reported from tracer tests are too high to be representative of local dispersivities. In fact they are equivalent dispersivities that represent dispersion between the measuring point and the injection point. Typical values for the local longitudinal dispersivity are probably on the order of  $10^{-2}$  to 1 m (Gelhar et al. [43], Matheron and DeMarsily [44], Gelhar and Axness [45]). Transverse dispersivity is smaller than longitudinal



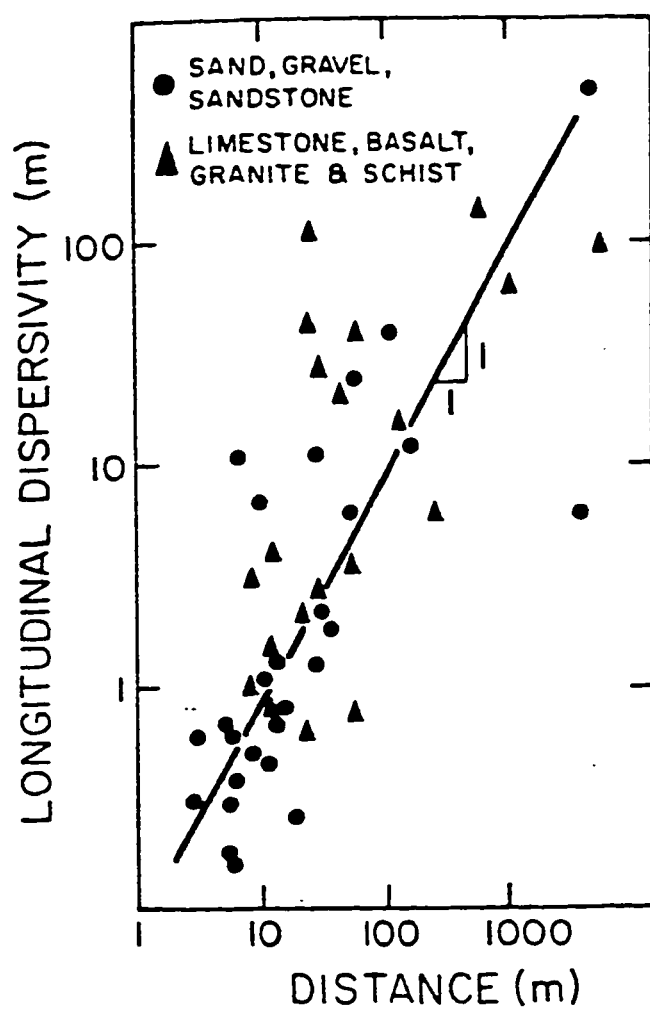


Fig. 3.5. Variation of Dispersivity with Distance.  
Source: Lallemant-Barres and Peaudecerf, (1978).

dispersivity; ratios of longitudinal to transverse dispersivity on the order of 10 to 100 have been suggested [41].

### 3.2.3 Theoretical Development of the Advection-Dispersion Equation for Solute Transport in Saturated Porous Media

The theoretical development of the advection-dispersion equation follows that of Bear [10], Ogata [17] and Lai and Jurinak [46]. It is assumed that the porous medium is homogeneous, isotropic, saturated, and that the flow is steady, and Darcy's law and Fick's laws of diffusion apply to problems of solute transport.

Under the Darcy assumption, the flow is described by the average linear velocity, which carries the dissolved substance by advection. In reality, there is an additional mixing process, hydrodynamic dispersion which is caused by variations in the microscopic velocity within each pore channel and from one channel to another. To describe the transport process on a macroscopic scale using macroscopic parameters, yet take into account the effect of microscopic mixing, it is necessary to introduce a second mechanism of transport, in addition to advection, to account for hydrodynamic dispersion.

To establish the mathematical statement of the conservation of mass, the solute flux into and out of a small elemental volume in the porous medium will be considered as shown in Figure 3.6. In Cartesian coordinates the specific discharge  $V$  has components  $(V_x, V_y, V_z)$  and the average linear velocity  $\bar{V} = V/n$  has components  $(\bar{V}_x, \bar{V}_y, \bar{V}_z)$ .

The rate of advective transport is equal to  $\bar{V}$ . The concentration of

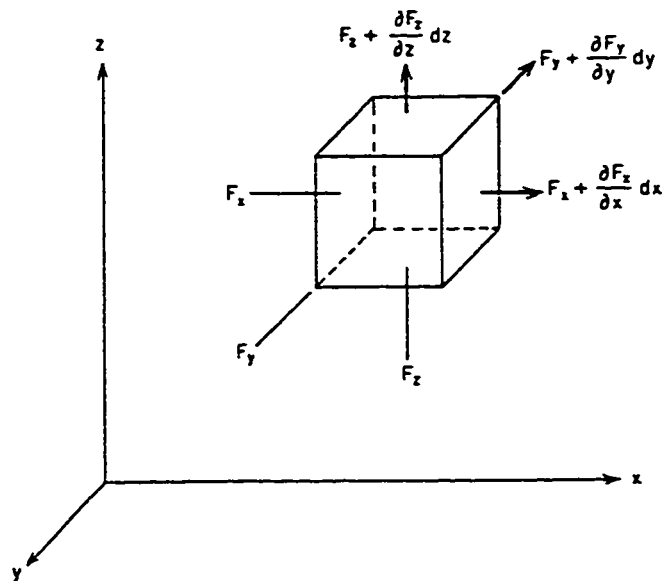


Fig. 3.6. Mass Balance in a Cubic Element in Space.  
 Source: R.A. Freeze and J.A. Cherry,  
 Groundwater (1979).

the solute  $C$  is defined as the mass of solute per unit volume of solution. The mass of solute per unit volume of porous media is therefore  $nC$ . For a homogeneous medium, the porosity  $n$  is a constant, and  $\frac{\partial}{\partial x}(nC) = n \frac{\partial C}{\partial x}$ . The mass of solute transported in the  $x$ -direction by the two mechanisms of solute transport can be represented as

$$\text{transport by advection} = \bar{V}_x nC \, dydz \quad (3.5)$$

$$\text{transport by dispersion} = -n D_x \frac{\partial C}{\partial x} \, dydz \quad (3.6)$$

where  $\bar{V}_x$  is the average linear velocity in the  $x$  direction,  $C$  is the mass of solute per unit volume of solution (concentration of solute),  $dydz$  is the elemental cross-sectional area of the cubic element, and  $D_x$ , the coefficient of hydrodynamic dispersion in the  $x$  direction, is the measure of the rate at which the concentration gradient  $\frac{\partial C}{\partial x}$  is dissipated. The negative sign before the dispersion term indicates that the contaminant moves toward the zone of lower concentration. The units of the two transport terms are in solute mass per unit time. The form of the dispersive component embodied in Eq. (3.6) is analogous to Fick's first law.

Assuming that these two components are linearly additive, and if  $F_x$  represents the solute flux per unit cross-sectional area transported in the  $x$  direction per unit time, then

$$F_x = \bar{V}_x nC - nD_x \frac{\partial C}{\partial x} \quad (3.7)$$

If the flux of solute is affected not only by advection and dispersion but also by geochemical reaction (i.e. adsorption or precipitation) within the unit cube then the mass balance equation must express the following condition:

net change of solute flux between inflow and outflow	=	<table border="0" style="width: 100%;"> <tr> <td style="width: 50%;">           rate of change of solute concentration inside the cubic element         </td> <td style="width: 10%; text-align: center;">+</td> <td style="width: 40%;">           rate of change of solute due to geochemical reactions         </td> </tr> </table>	rate of change of solute concentration inside the cubic element	+	rate of change of solute due to geochemical reactions
rate of change of solute concentration inside the cubic element	+	rate of change of solute due to geochemical reactions			
		(3.8)			

The two rate terms on the right hand side of Eq. (3.8) are given by  $\partial C/\partial t$  and  $\partial S/\partial t$  where  $S$  is the amount of solute adsorbed or precipitated or biologically degraded per unit mass of the porous medium. Eq. (3.8) can be written,

$$dydz \left[ \left( -nD_x \frac{\partial C}{\partial x} + n\bar{V}_x C \right)_x - \left( -nD_x \frac{\partial C}{\partial x} + n\bar{V}_x C \right)_{x+dx} \right] =$$

$$(ndxdydz) \frac{\partial C}{\partial t} + (dxdydz) \rho_b \frac{\partial S}{\partial t} \quad (3.9)$$

where  $n$  is the porosity and  $\rho_b$  is the bulk density (mass/volume).

The subscripts  $x$  and  $x+dx$  refer to the flux into the cubic element at plane  $x$  and out of the element at plane  $x+dx$ .

Dividing both sides by  $(ndxdydz)$ , i.e. assuming porosity is everywhere constant,

$$\frac{[(D_x \frac{\partial C}{\partial x} - \bar{V}_x C)_{x+dx} - (D_x \frac{\partial C}{\partial x} - \bar{V}_x C)_x]}{dx} = \frac{\partial C}{\partial t} + \frac{\rho_b}{n} \frac{\partial S}{\partial t} \quad (3.10)$$

which is equivalent to the partial differential equation

$$\frac{\partial}{\partial x} (D_x \frac{\partial C}{\partial x} - \bar{V}_x C) = \frac{\partial C}{\partial t} + \frac{\rho_b}{n} \frac{\partial S}{\partial t} \quad (3.11)$$

Assuming that  $D_x$  is independent of position in the  $x$  direction, and that the average linear velocity,  $\bar{V}_x$ , is constant, Eq (3.11) can be written,

$$D_x \frac{\partial^2 C}{\partial x^2} - \bar{V}_x \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} + \frac{\rho_b}{n} \frac{\partial S}{\partial t} \quad (3.12)$$

Rearranging terms

$$D_x \frac{\partial^2 C}{\partial x^2} - \bar{V}_x \frac{\partial C}{\partial x} - \frac{\rho_b}{n} \frac{\partial S}{\partial t} = \frac{\partial C}{\partial t} \quad (3.13)$$

When considering two or three dimensional cases, one of the fundamental aspects of dispersion becomes apparent: it is not an isotropic process, even if the medium itself is homogeneous and isotropic.

The coefficient of dispersion is regarded as a symmetric tensor, the direction of the velocity being the principal direction of this tensor. Along this direction, the coefficient of dispersion is referred to as the coefficient of longitudinal dispersion, and coefficient of transverse dispersion is used for the two other directions orthogonal to

the direction of the velocity. Mechanical dispersion is one or two orders of magnitude greater in the average direction of the velocity in the porous medium than in any direction normal to this velocity.

In the case where the velocity, and the coefficient of dispersion are constant, and if  $x$  is the direction of the velocity, the three dimensional advection-dispersion equation may be written as:

$$D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} - \bar{V}_x \frac{\partial C}{\partial x} - \frac{\rho_b}{n} \frac{\partial S}{\partial t} = \frac{\partial C}{\partial t} \quad (3.14)$$

$D_x$  is the coefficient of longitudinal dispersion ( $L^2/T$ )

$D_y = D_z$  is the coefficient of transverse dispersion ( $L^2/T$ )

If the velocity and the coefficient of dispersion are not constant, the equation is written:

$$\text{div}(\underline{D} \text{ grad } C - \frac{\bar{V}}{\bar{V}} C) = \frac{\partial C}{\partial t} \quad (3.15)$$

where  $\text{div} = \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}$

$\underline{D}$  is the dispersion tensor

$\text{grad}$  is a vector of components  $\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}$

$\frac{\bar{V}}{\bar{V}}$  is the velocity vector

In this study, a two-dimensional saturated porous medium with steady, uniform flow in the x direction is considered. The equation describing the transport is given by,

$$D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} - \bar{V}_x \frac{\partial C}{\partial x} - \frac{\rho_b}{n} \frac{\partial S}{\partial t} = \frac{\partial C}{\partial t} \quad (3.16)$$

#### 3.2.4 Adsorption in Advective-Dispersive Systems

Adsorption of trace organics to soil organic matter is generally proposed to be the primary physicochemical mechanism for altering the fate of such organics in saturated groundwater flow.

Adsorption is usually incorporated into the advection-dispersion equation in a manner based on the assumption that the concentration of the contaminant in the solution phase (S) is a function of the concentration in the solid phase (C) [41], or

$$S = f(C) \quad (3.17)$$

It is important to recognize that Eq. (3.17) is based on the assumption that equilibrium conditions exist between the solution-phase and solid-phase concentrations.

In some situations, the relation between S and C is linear, and thus the slope of the partitioning function becomes a constant and is generally referred to as the distribution coefficient  $K_d$ . A chromatographic partitioning process is commonly used in soil studies to model the average velocity of a compound,  $V_C$ , relative to the average



velocity of water,  $\bar{V}$ . Applying the theory of chromatography to saturated groundwater systems [47], the ratio,  $R$ , the retardation factor is equal to  $\bar{V}/V_C$ , and can be shown to be approximately:

$$R = \frac{\bar{V}}{V_C} = (1 + \frac{\rho_b}{n} K_d) \quad (3.18)$$

where  $\rho_b$  = bulk density of the medium,  $n$  = porosity, and  $K_d$  = ( $\mu\text{g}$  of compound/g-soil phase)/ ( $\mu\text{g}$  of compound/ml-water phase)

The retardation factor  $R$  and the use of the distribution coefficient in the advection-dispersion equation was introduced by Higgins [48] into the literature on contaminant migration in groundwater.

The  $S = f(C)$  relation is normally determined in the laboratory by means of batch tests in which a known mass of the porous medium is immersed in a solution of known contaminant concentration. After leaving the liquid-solid mixture for a period of hours, the contaminant concentration in solution is determined and, by difference, the concentration absorbed on the solids is known. When this test is repeated at constant temperature using different concentrations of the contaminant in solution, the  $S = f(C)$  relation, which is known as the adsorption isotherm, is obtained.

There are many possible functional forms of adsorption isotherms, a large number of which are described by Smith [49]. However, in studies of trace-level contaminants in geologic media, isot-

herms from batch tests usually fit closely to a functional relation known as the Freundlich isotherm,

$$S = kC^a \quad (3.19)$$

where  $k$  and  $a$  are empirical coefficients. If  $a = 1$ , the isotherm is linear, then  $k = K_d$  and Eq. (3.18) is applicable. If  $a > 1$  the concentration versus distance profile in the flow direction is narrow and the contaminant mass in solution advances less rapidly than would be the case for linear adsorption. If  $a < 1$  the concentration profile is broad and the contaminant mass in solution advances more rapidly than in the linear case.

For a linear isotherm,

$$S = K_d C \quad (3.20)$$

$$\frac{\partial S}{\partial t} = K_d \frac{\partial C}{\partial t} \quad (3.21)$$

Substituting Eq. (3.21) in Eq. (3.16) we have

$$D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} - \bar{V}_x \frac{\partial C}{\partial x} - \frac{\rho_b}{n} K_d \frac{\partial C}{\partial t} = \frac{\partial C}{\partial t}$$

Rearranging terms

$$D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} - \bar{V}_x \frac{\partial C}{\partial x} = (1 + \frac{\rho_b}{n} K_d) \frac{\partial C}{\partial t} \quad (3.22)$$

Substituting Eq. (3.18) in Eq. (3.22) we have

$$D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} - \bar{V}_x \frac{\partial C}{\partial x} = R \frac{\partial C}{\partial t} \quad (3.23)$$

Chiou et al. [50], Karickhoff et al. [51], Means et al. [52], Schwarzenbach and Westall [53] have reported that adsorption of various nonionic organic solutes at trace concentrations onto soils follow an essentially linear isotherm and are readily reversible. When adsorption is solely due to the organic carbon content of the soil, the partition coefficient is expressed as  $K_{oc}$ , where  $K_{oc} = \frac{K_d}{f_{oc}}$ , with  $f_{oc}$  being the weight percent of solid-phase organic carbon.

The methods of calculating  $K_d$  are primarily based on the organic carbon content of the soil. Pioneering work of Lambert [54,55,56] and co-workers (Lambert et al. [57]) has demonstrated that adsorption of neutral organic pesticides is correlated with the natural carbon content of a given soil. Lambert also suggested that the role of organic matter is similar to that of an organic solvent in a solvent extraction process. Thus, partitioning of a neutral organic compound between soil organic matter and water should correlate well with its partitioning between water and an immiscible organic solvent.

Chiou et al. [50] showed that the transfer of nonionic organic compounds from water to soil could be due to partitioning in the soil organic matter. They demonstrated linear adsorption isotherms over a wide range of concentrations.

Karickhoff et al. [51] investigated the role of particle size and

organic matter on adsorption of a number of aromatic and chlorinated hydrocarbons. The correlation of adsorption with sorbate aqueous solubility and octanol/water distribution coefficient was also studied by Schwarzenbach and Westall [53].

A promising relationship between  $K_{oc}$  and structural chemical properties of organic compounds has been developed, which permits the estimation of  $K_{oc}$  or  $K_d$  to within a factor of 10 or better for most nonpolar organic compounds. This relationship, which involves the use of partition coefficients for mixtures of water and octanol, has been established for soils in which the organic carbon content exceeds 0.1 percent.

The development of this approach is revised by Hansch and Leo [58] and others. A linear relationship exists for partitioning of organic solutes between sedimentary organic matter and groundwater and for partitioning between octanol and water. The octanol/water system can be used as a surrogate for the real groundwater system in describing relative partition coefficients. The following relationships have been observed for various organic solute/sediment system when the organic carbon content is greater than 0.1% :

Karickhoff et al. [51]

$$\log K_{oc} = 1.00 \log K_{ow} - 0.21 \quad (3.24)$$

Schwarzenbach and Westall [53]

$$\log K_{oc} = 0.72 \log K_{ow} + 0.49 \quad (3.25)$$

Means et al [52]

$$\log K_{oc} = 2.00 \log K_{ow} - 0.317 \quad (3.26)$$

where  $K_{ow}$  is the octanol/water partition coefficient, values of which can be obtained from Leo et al. [59] or Hansch and Leo [58]. The variation in the slope parameter is due to differences in soil organic matter or to differences in the organic solutes investigated.

## CHAPTER 4

### 4. EXPERIMENTAL PROCEDURE

#### 4.1 Purpose

In order to determine the longitudinal and lateral dispersion coefficients for the contaminant in question, and to predict the development of the contaminant plume variation with respect to space and time an experimental plexiglass model was set up in the laboratory. Each experiment involved the creation of a contaminant plume under controlled laboratory conditions as detailed in the following sections.

In each experiment a constant uniform flow through a porous medium of known hydraulic characteristics: coefficient of permeability  $K$ , porosity  $n$ , and specific discharge  $V$  was established. A contaminant of known source characteristics: volumetric flow rate  $q$ , and initial concentration  $C_0$  was introduced, and the concentration variation along the direction and perpendicular to the direction of flow were measured at regular time intervals. Using these results the longitudinal and lateral dispersion coefficients were computed. The parameters  $C_0$  and  $V$  were varied in each experiment.

#### 4.2 Construction of the Plexiglass Sand Box Model

Five 13 mm thick sheets of plexiglass 182 cm by 124 cm were used in the construction of the model. All five sheets of plexiglass were machined along the four edges in order to obtain a smooth fin-

ish and a tight fit when placed in position. Two sheets of plexiglass were used for the bottom of the box while another two sheets were used for the cover of the box. The fifth sheet was used for the longer and shorter vertical sides of the box. The outer dimensions of the plexiglass box was 358.4 cm by 125.4 cm by 17.8 cm.

In assembling the plexiglass box the following procedure was adopted. Silicon sealant was applied at the joints and into the drilled holes. After allowing the silicon sealant to stand for about 3 to 5 min, the counter sunk screws were tightened, and once again sealant was applied at the joints to provide a good seal and to overcome the problem of leakage. A photographic representation of the plexiglass box is shown in Figure 4.1.

Approximately 61 cm from the side and 9 cm from the bottom of each of the shorter vertical sides a 9.5 mm diameter hole was made, as shown in Figure 4.1. A hollow plexiglass tube was fixed to the hole to facilitate the connection of the 9.5 mm diameter reinforced tygon tube from the inflow and outflow constant head tanks.

Approximately 15.3 cm from each end of the box, a glass wool screen extended across the width of the tank. The glass wool screen was fabricated in the laboratory. Two 6 mm thick sheets of plexiglass, 122.8 cm by 15.2 cm were taken and holes were perforated at equally spaced intervals. The glass wool was placed in between these two pieces of plexiglass and small brass screws held the plexiglass, sandwiching the glass wool. This arrangement consisted of the glass wool screen. The screen was then placed across the width of the

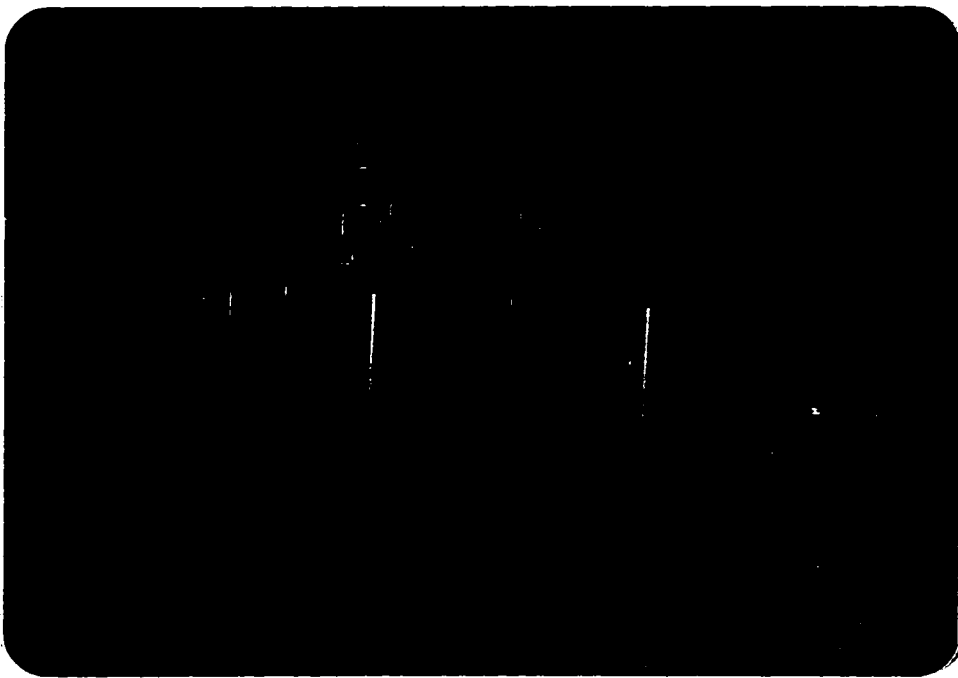


Fig. 4.1. A Photographic representation of the Plexiglass Box.



box, by sliding the screen into the groove that was made in the longer vertical sides of the box. To hold the screen further in position sealant was applied in between the groove and the screen. Furthermore, at the bottom, where the screen touched the box sealant was applied to prevent the water from flowing beneath the screen. To prevent the screen from bowing out, when the plexiglass box was filled with sand four pieces of plexiglass supports with perforations were placed at equal distances along its length. Each piece was kept in position by applying sealant along the three edges of the support. A similar arrangement was made at the downstream end of the box. This screen confines the sand medium and provides inflow and outflow chambers which distribute the incoming and outgoing flows uniformly across the width of the box. Figure 4.2 shows the glass wool screens placed in position.

The inlet for the contaminant was at a distance approximately 7.6 cm from the upstream glass wool screen. This device consisted of a hollow 25.4 mm plexiglass tube fixed to the bottom of the box on the center line. This tube had a 0.79 mm slit along its length and was placed in such a way that it faced the downstream direction, as shown in Figure 4.3. Furthermore, once the cover of the box was placed, 3.8 cm of the hollow tube protruded outside to facilitate the injection of the contaminant solution.

### 4.3 Sampling Ports

On the bottom of the box, as shown in Figure 4.4, seventy

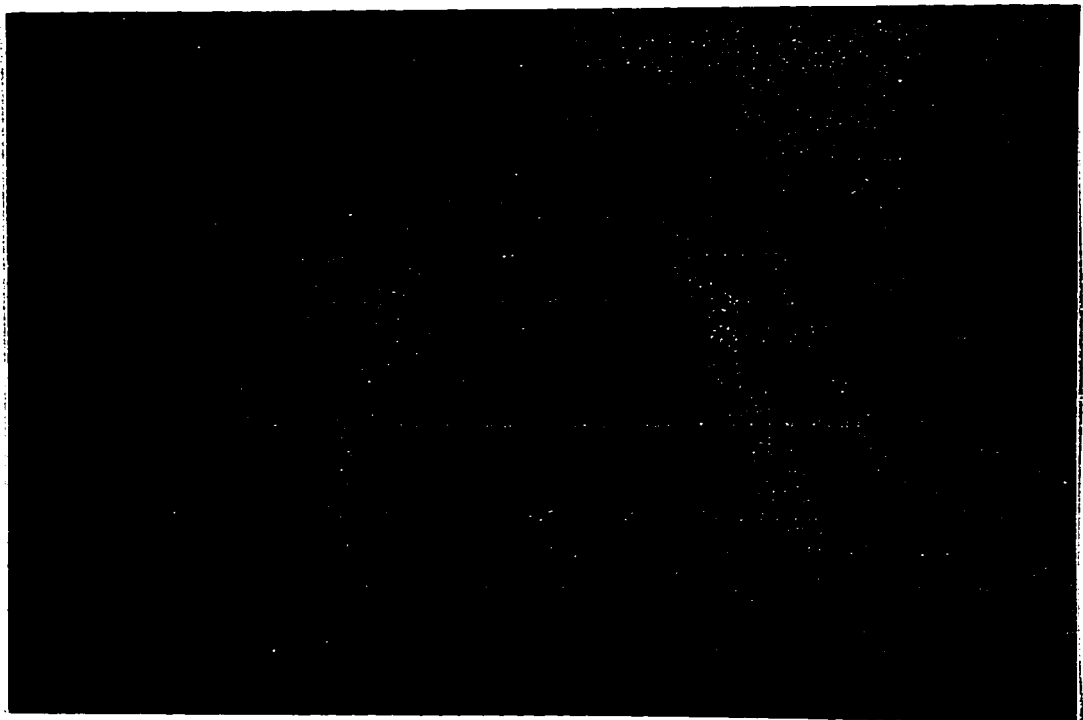


Fig. 4.2. A Photographic representation of the Glass Wool Screens placed in position.

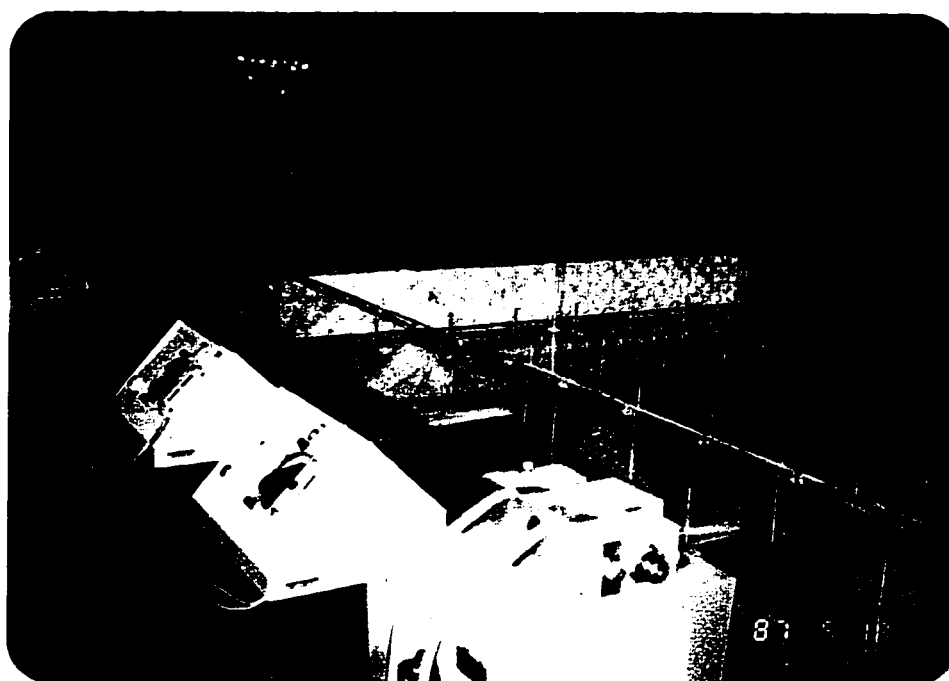


Fig. 4.3. A Photographic representation of the Hollow Plexiglass Tube fixed to the bottom of the box on the center line.

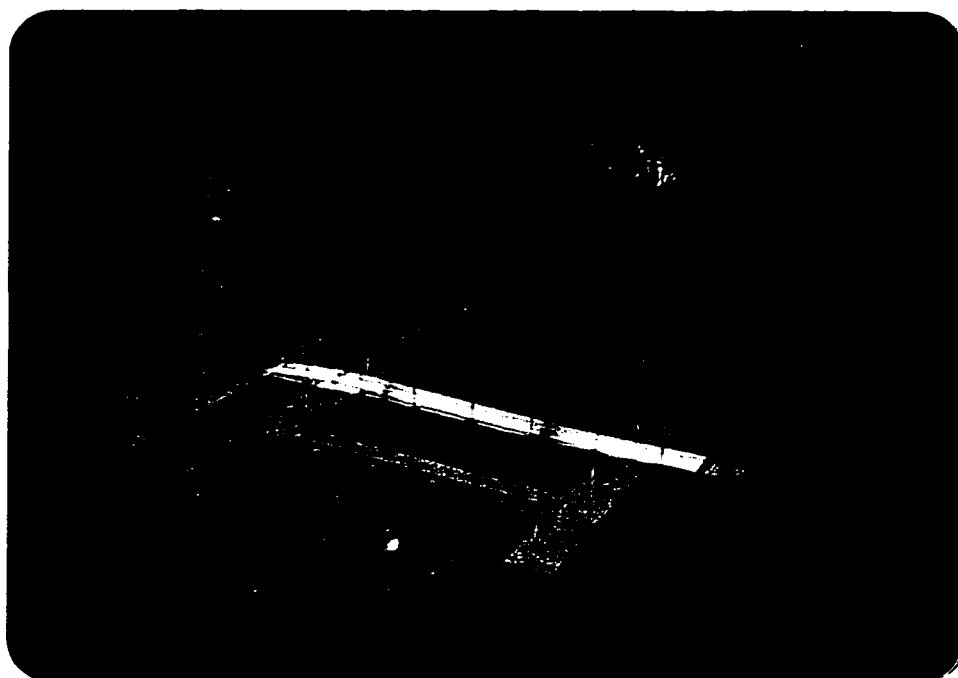


Fig. 4.4. A Photographic representation of the Sampling Ports provided for extracting fluid samples from the porous medium.

seven sampling ports were provided for extracting fluid samples from the porous media. The ports were arranged in seven rows with 11 ports in each row. The spacing between rows was 15.3 cm and the spacing within a row was 30.5 cm. The ports in all the rows contained a sampling tube, each, which penetrated 6.3 cm into the porous medium.

The sampling tubes were hollow stainless steel tubes, 12.7 cm long with an outside diameter of 3 mm. The sampling tubes were placed in position by making a hole in the bottom of the plexiglass box with a 3 mm drill, and then forcing the stainless steel tube in, making sure 6.3 cm protruded inside the box. Once this was done, silicon sealant was applied both from inside and outside the bottom of the box to prevent leaking. A piece of tygon tube was dipped in hot water to make the edge of the tygon tube flexible, and then the tygon tube was pushed into the protruding end of the stainless steel tube that was outside the box. The other end of the tygon tube was clamped with a Hoffmann screw to prevent leaking, as shown in Figure 4.5.

Sand was placed into the empty box in layers of approximately 3 cm. Sieve Analysis of the sand used in the experiment is provided in the Appendix. With the placement of each layer, the sand was hand rodded and tamped to achieve a high degree of consolidation. When a depth of approximately 5 cm of sand was placed in the plexiglass box, to prevent sand from clogging the diameter of the sampling tube, a small piece of glass wool was placed on the top of each

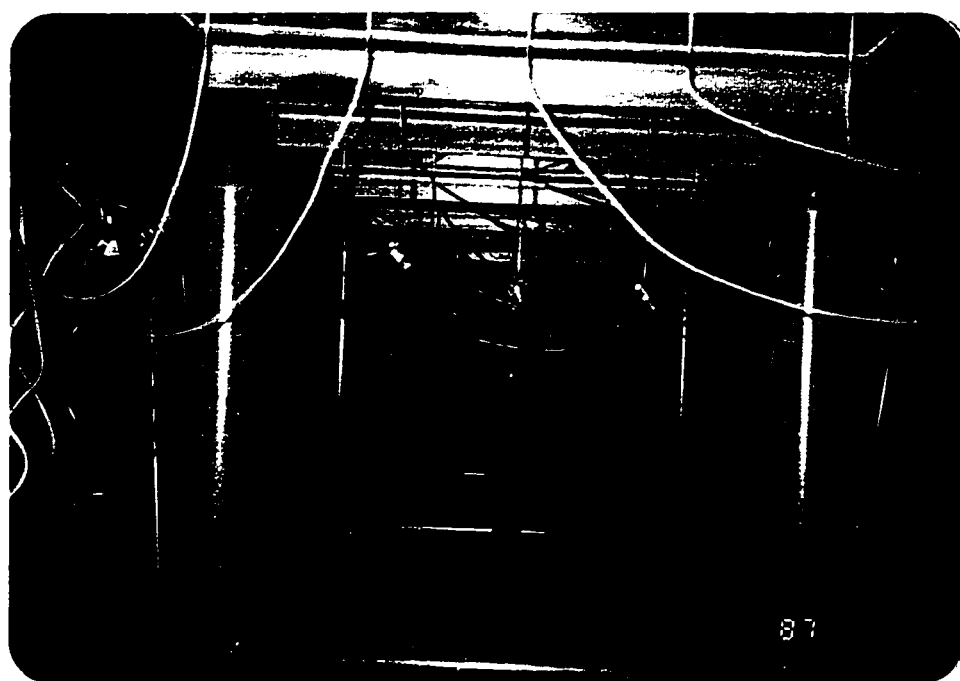


Fig. 4.5. A Photographic representation of the Sampling Ports connected to Tygon Tubes and clamped with Hoffmann Screws.

tube and the sand was placed on top of the glass wool. Once the box was filled to the top with sand, water was slowly passed into the box. When it was observed that the sand was saturated with water, the box was left open for a period of time and gently rodded and tapped to allow any entrained air to escape. A layer of glass wool was soaked in water and then placed over the top of the sand. This was done to prevent any water moving in between the plexiglass and the top of the media. Before placing the cover of the box, sealant was applied at the joints and into the drilled holes. The cover of the box was placed in position and then the counter sunk screws were tightened. Finally in order to prevent leaking sealant was applied right around the box at all joints. A photographic representation of the plexiglass box filled with sand is shown in Figure 4.6.

#### 4.4 Manometer Board

Nine piezometer ports were located along the cover of the box. They were placed in three rows with three ports in a row. A hollow stainless steel tube bent in the form of a L shape was inserted into a rubber stopper that plugged the hole in the plexiglass. One end of the tube was buried in the porous medium while the other end of the tube was connected via a flexible vinyl tube to a manometer board. The manometer board consisted of seven, 1.5 m long glass tubes fastened to a board, as shown in Figure 4.7. To facilitate the reading of the water level a scale was attached to the board by the side of each tube. The board was mounted on a steel frame which had the



Fig. 4.6. A Photographic representation of the Plexiglass Box filled with Sand.



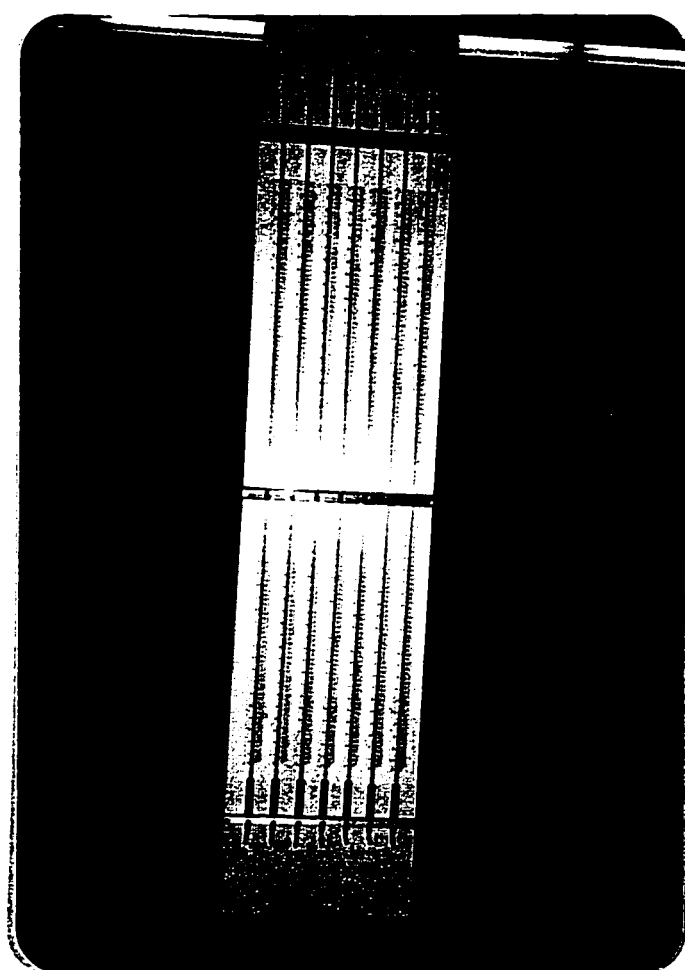


Fig. 4.7. A Photographic representation of a Manometer Board.

provision of sliding the board in the upward and downward directions. The piezometers were used to determine the uniformity of the flow and the magnitude of the hydraulic conductivity of the medium.

#### 4.5 Construction of the Steel Frame

A steel frame with peripheral dimensions 360 cm by 127 cm was built of 50 mm x 50 mm angle iron, as shown in Figure 4.8. All the joints in the construction of the steel frame were welded. As a finish one coat of red oxide was applied, followed by two coats of blue enamel paint. To provide bracing for the cover of the plexiglass box when filled, four small steel plates were welded to the peripheral 50 mm x 50 mm angle iron frame at equally spaced distances on both sides. A steel rod with a bolt and nut arrangement was connected to this plate. The other end of the rod passed through a steel tube which was placed across the width of the cover of the plexiglass box. The other end of the tube was connected in a similar manner to the steel plate with a bolt and nut arrangement, on the other side. In this manner four cross bars braced the cover of the plexiglass box which prevented it from bulging due to the water pressure.

#### 4.6 Inflow and Outflow Arrangements

To maintain a saturated porous media, and to keep the system under a small positive pressure head, constant head tanks were used on either end of the plexiglass box, as shown in Figure 4.9. Also, the constant head tanks controlled the steady flow of water through

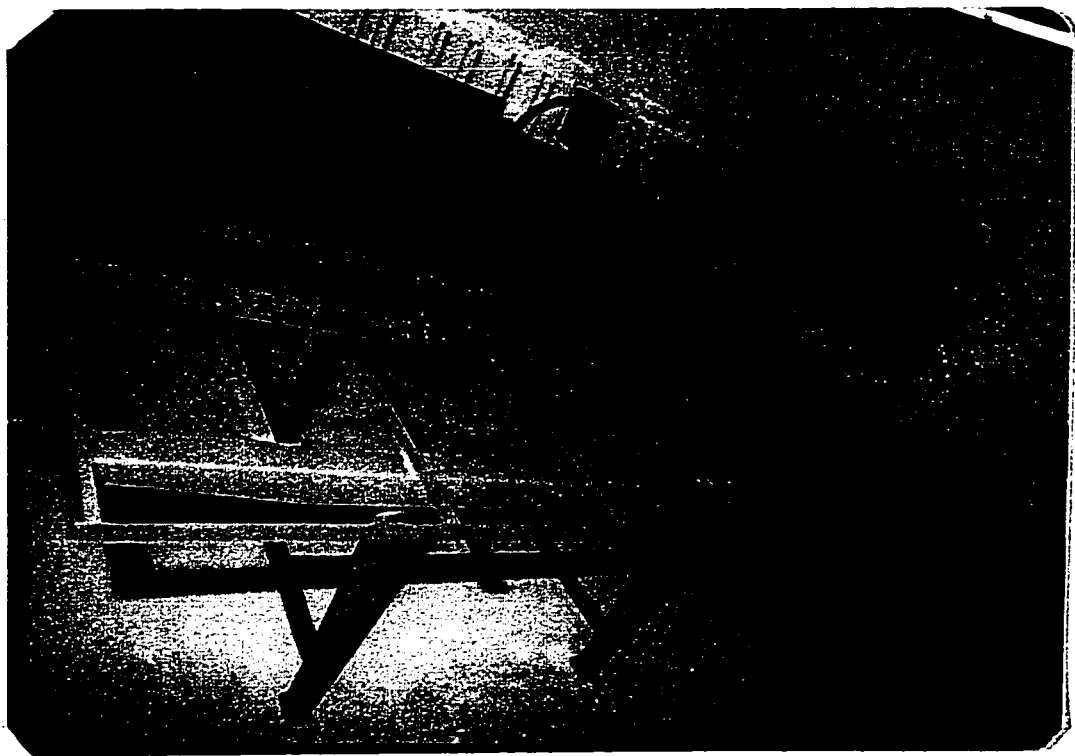


Fig. 4.8. A Photographic representation of the Steel Frame.

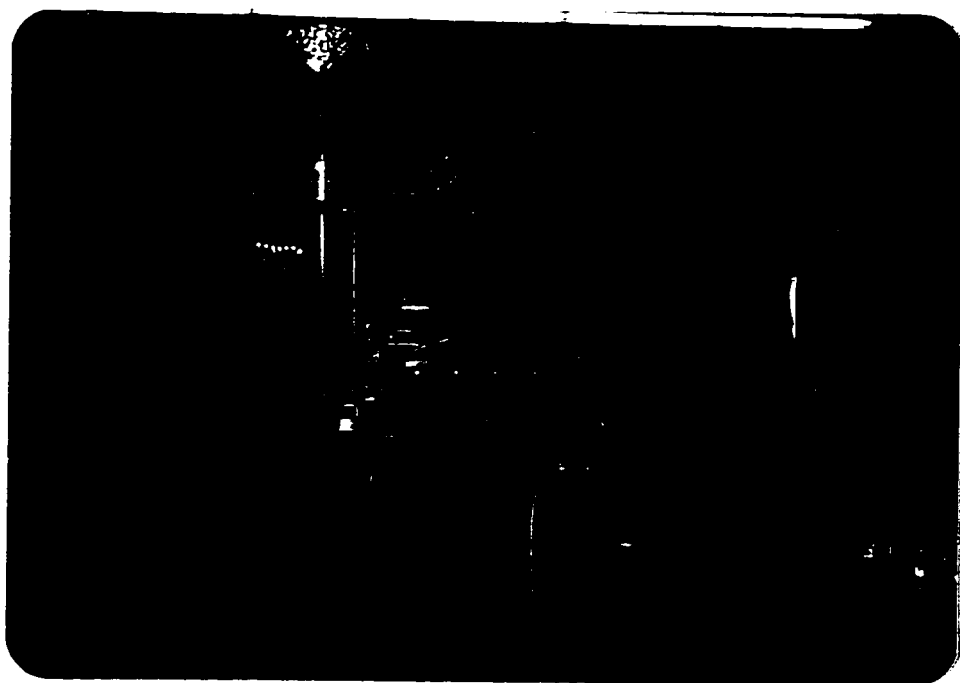


Fig. 4.9. A Photographic representation of the Constant Head Tanks connected to the Plexiglass Box.

the medium.

The water supply for the experiment was contained in a 200 litre plastic container. A supply pump delivered the water from the plastic container to the inflow constant head tank via a 9.5 mm internal diameter reinforced tygon tube. A gate valve was provided in this tube to regulate the inflow into the constant head tank. The overflow from the constant head tank returned to the 200 litre plastic container via a 19.0 mm internal diameter reinforced tygon tube. The remaining flow was supplied under constant head to the water chamber at the upstream end of the box, through a 9.5 mm internal diameter reinforced tygon tube. Here too, a gate valve was provided to regulate the inflow into the water chamber.

Water left the box in a similar manner as it entered, passing through the water chamber at the downstream end of the box, and then into the outflow constant head tank and discharging into the drain.

Two small holes were made in the upstream and downstream water chambers for bleeding purposes. By this procedure the air entrapped inside the box was relieved. Once the water was filled, two rubber stoppers were used to plug these holes.

A graduated cylinder with a stop watch was used to measure the flow rate at the discharge end from the outflow constant head tank.

#### 4.7 Contaminant Source Injected

Chloroform solution was selected as the contaminant source because it is a known carcinogen present in groundwater. For the slug input of the contaminant solution, a known volume of the contaminant was injected using a syringe into the medium through the hollow plexiglass tube protruding from the cover of the box. Once this was done the hollow plexiglass tube was plugged with a rubber stopper.

For the continuous input of the contaminant solution, a third over head tank was used. This tank was made out of a 25.4 cm outer diameter plexiglass hollow tube. A circular base made out of plexiglass was fixed to the hollow plexiglass tube, and an opening was made in the base to fix a 9.5 mm internal diameter reinforced tygon tube. A gate valve was provided to regulate the flow of the contaminant solution into the porous medium. The other end of the reinforced tygon tube was connected to the hollow plexiglass tube protruding from the cover of the box. A photographic representation of the complete setup is shown in Figure 4.10.

#### 4.8 Typical Slug Input Experiment

The 200 litre plastic container was filled with tap water and allowed to stand. The supply pump was started and the water was allowed to fill into the constant head tanks, while keeping the gate valves open. By regulating the opening of the gate valves and adjusting the heights of the inflow and outflow constant head water

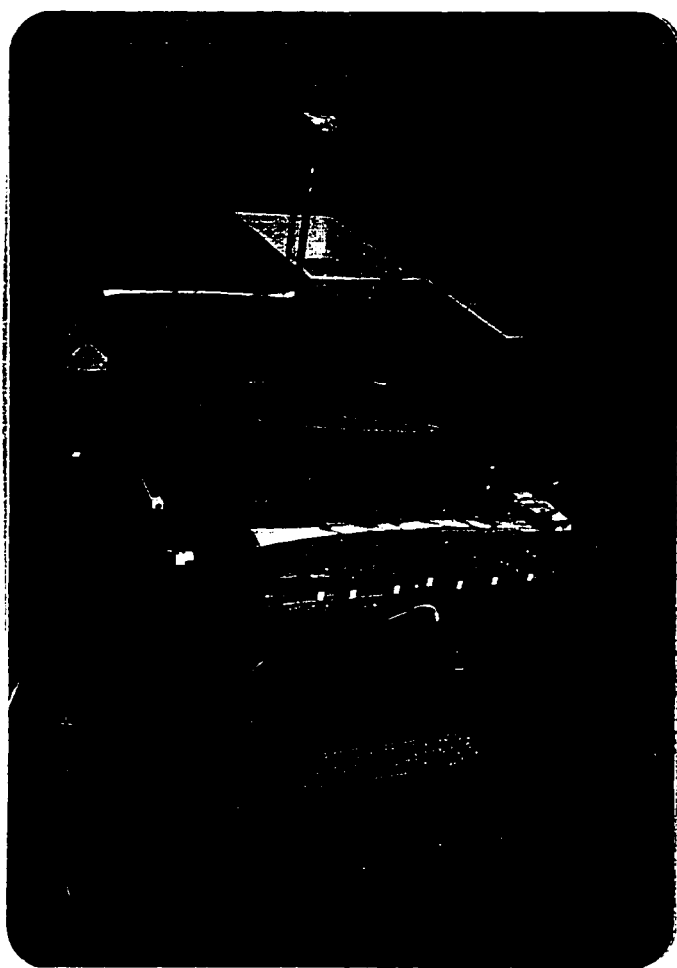


Fig. 4.10. A Photographic representation of the complete Setup.

tanks, a desired flow rate was established in the medium.

One litre of chloroform solution of known concentration was prepared and placed in a volumetric flask. (Preparation of chloroform solution is given in the Appendix). A known volume of this solution was taken in a syringe and injected through the hollow plexiglass tube protruding from the cover of the box into the medium.

In order to determine the flow rate, the overflow from the outlet constant head tank was measured with a graduated cylinder and a stop watch. The known cross section of the tank then allowed for the determination of the specific discharge  $V$ . Piezometric heads were observed in the manometer board, from which the hydraulic conductivity,  $K$ , of the medium was calculated.

The system was left undisturbed while the plume developed. Sampling was begun after 45 min, or 1 hr. Before the collection of a sample from the port, the Hoffmann screw was released and approximately 5 ml of the sample was withdrawn and discarded. This procedure was adopted so that the sample collected was a representative sample from the medium and not a sample that remained in the stainless steel and tygon tube. In some experiments samples were taken at a particular location along the center line along the direction of flow (fixed  $x$  location and  $y = 0$ ) at regular time intervals of 45 min, 1.5 hr, 2.5 hr, 3.5 hr, 4.5 hr, 5.5 hr, 6 hr, and so on. In other experiments samples were taken along the center line at all  $x$  locations instantaneously at regular time intervals. In another experiment samples were taken at a particular  $x$  location, and different  $y$  loca-



tions instantaneously at regular intervals of time.

Samples were collected in glass bottles by releasing the Hoffmann screws. When approximately 10 ml to 15 ml of the sample was collected the glass bottles were closed air tight or sealed immediately. This procedure was adopted in order to make sure that the chloroform present in the sample did not volatilize. The samples were then prepared for gas chromatographic analysis. In case where preparation for analysis was not possible on the same day, the samples were preserved in the refrigerator. Prepared samples, extracted in pentane as a solvent, were taken to the Research Institute (KFUPM) for gas chromatographic analysis. Where analysis of extracted samples in pentane were not possible on the same day, the extracted samples were preserved in the freezer.

In between each experiment water was passed through the media for about 5 to 6 hr in order to flush the system of the contaminant. In doing this it was possible to remove traces of chloroform that remained in the media during an experiment.

#### **4.9 Typical Continuous Input Experiment**

For the continuous input experiment 20 to 25 l of chloroform solution of known concentration was prepared and placed in the third overhead tank, as shown in Figure 4.11. The flow rate of the chloroform solution was determined by knowing the volume passed into the medium during the course of the experiment.

The system was left undisturbed while the plume developed.



Fig. 4.11. A Photographic representation of the Third Over Head Tank containing the Chloroform solution.

Sampling was begun after 45 min. Here too, before the collection of a sample the port was flushed in order to obtain a representative sample and not a sample that remained in the stainless steel and tygon tube. In the experiment samples were collected instantaneously at five different  $x$  locations and at each  $x$  location five ports were sampled, two ports on either side of the center line and one on the center line. The procedure in which samples were collected, prepared for analysis, and preserved were the same as that for the slug input experiment.

#### 4.10 Gas Chromatography Instrumentation

Tswett [60] has defined : "Chromatography" as a method in which the components of a mixture are separated on an absorbent column in a flowing system. Recently the International Union of Pure and Applied Chemistry has defined chromatography as: "A method used primarily for the separation of the components of a sample, in which the components are distributed between two phases, one of which is stationary while the other moves. The stationary phase may be a solid, or a liquid supported on a solid, or a gel. The stationary phase may be packed in a column, spread as a layer, or distributed as a film, etc., in these definitions "chromatographic bed" is used as a general term to denote any of the different forms in which the stationary phase may be used. The mobile phase may be gaseous or liquid [61,62]."

The instrumentation for Gas Chromatography (GC) incorporates

the features common to all forms of chromatography, namely a mobile phase, a stationary phase and a detection system. GC utilizes a column containing the stationary phase, but requires a gaseous mobile phase, the carrier gas, and a sample introduction or injection system. The detectors require an amplifier for signal processing; the variable parameters, for example, column and injection temperature, are electronically controlled. The GC used for the analysis of samples collected in the experiment was a HP 5880A Gas Chromatograph and consisted of the following components.

1. Carrier gas supply and controls;
2. Sample introduction/injector system;
3. Chromatographic column and oven;
4. Detector
5. Amplifier and signal processing, and control electronics.

#### 4.11 Sample Preparation for Gas Chromatographic Analysis

For the purposes of preparing samples for the gas chromatographic analysis, Liquid-Liquid Extraction (LLE) [63] method was used for the extraction of chloroform from the water samples using pentane as a solvent.

The procedure adopted to extract the sample was as follows: 10 ml of the water sample was pipetted into an extraction vessel. Then 2 ml of pentane was taken in another pipette and emptied in the same extraction vessel. The next step involved the vigorous mixing of the pentane and the water sample for approximately 5 to 6 min-

utes. In order to accomplish this a vortex mixer was used. When this was done the extraction vessel was left aside for a few minutes, until a clear separation of the pentane and the sample was visible. A 500  $\mu$ l automatic pipette was used to pipette out the top layer of pentane from the water sample into a vial. The vials were numbered and kept aside. When extracted samples were unable to be analyzed on the same day, they were preserved in the freezer in the Environmental Engineering Laboratory for analysis on the following day. All glassware were washed with water, and then with distilled water and followed by rinsing with pentane before a sample was prepared.

#### 4.12 Analysis of Samples on the Gas Chromatograph

Analysis of chloroform in pentane were performed on a HP 5880A Gas Chromatograph equipped with an auto-sampler, utilizing a Ni63 Electron Capture Detector and a HP 5880A Model Integrator. A 30 m long fused silica capillary column, 0.254 mm I.D., coated with a film of stationary phase (0.25  $\mu$ m) DB-5 was used for the chromatographic separation of the chloroform in pentane. The GC oven temperature was programmed from 35°C to 50°C at a ramp rate of 5°C/min with an initial hold time of 2 min. Nitrogen gas was used as the carrier gas and make-up gas at flow rates of 1.5 ml/min and 60 ml/min. The detector and injection port temperatures were 300°C and 270°C respectively. Chloroform was detected at a retention time (Rt) of 2.45 +/- 0.02 min.

Standard solutions of chloroform in pentane ranging in concen-

trations between 25 ppb and 150 ppb were analysed. In order to obtain a calibration curve, for each standard solution three runs were performed. The average of three runs for each sample were taken for the plotting of the calibration curve. A calibration curve was established with a linear relation of  $R^2 = 0.998$ . The unknown 39 samples obtained from an experiment analysed in the expected concentration range of 25 ppb to 150 ppb were found to be low and outside the desired range.

After reviewing the system dynamics, the original dose of chloroform injected in the form of a contaminant was increased. Another set of standard solutions of chloroform in pentane ranging in concentrations between 250 ppb and 2500 ppb were analysed.

During the course of the experiments, samples were collected and extracted following the procedure mentioned earlier. All the samples extracted in the vials were placed in an automatic sampler, and the GC was programmed according to the specifications given earlier. In order to maintain a record of the analysis, each vial was given an identification number.

#### 4.13 Distribution Coefficient $K_d$ for Chloroform

The distribution coefficient  $K_d$  incorporated in the advection-dispersion equation was determined in the laboratory by performing some simple column experiments. As a first step, three 25 ml burettes were taken, and mounted vertically on three stands. Ini-

tially a known volume of chloroform solution of a known concentration was taken and approximately half of the burette was filled with this solution. In the next step a known mass of the sand used in the experiment was taken and the burette column was gradually packed with sand. To achieve a high degree of compaction, the walls of the burette were tamped while packing. A head of 4 cm chloroform solution was maintained in the burette. To prevent the chloroform evaporating from the solution the top of the burette was sealed. Knowing the volume of chloroform that was left, the volume used in the experiment was determined. Similarly knowing the mass of sand left, the mass of sand used in the experiment was determined. The experiment was allowed to stand for 6 hr. This time interval was adopted since the sand box experiments were conducted for 6 hr. The other two burettes were packed in a similar manner, the only change being that different concentrations of chloroform solution was used.

After about 6 hr a sample from each of the three experiments were collected. At the beginning of the sampling process an initial volume of approximately 5 ml was collected and discarded. This flushing was done in order to collect a representative sample from the medium and not a sample that was collected at the tip of the burette.

The samples were sealed to prevent the chloroform from evaporating. Since the initial concentrations used were high in the ppm range, 1 ml of the sample was taken and diluted in 999 ml of water to form a 1 l solution. This was done for all the influent and effluent

samples. The preparation of the samples for the GC analysis was done in the same manner as described in the previous section.



## CHAPTER 5

### 5. RESULTS AND DISCUSSION

Analytical models are developed by solving the advection-dispersion equation for certain simplified boundary and initial conditions. Numerous solutions are available in the literature (Bear [64], Hunt [33], Wilson and Miller [34], Cleary and Adrian [65], and Shen [32]) for slug and continuous contaminant sources with boundary conditions ranging from homogeneous confined aquifers to infinite thickness water table systems.

Although there are a variety of analytical solutions to pollution problems available many are not presented in a form convenient to the user. The 2-D analytical model developed by Hunt [33], and Wilson and Miller [34] is one of the simplest to use and can account for longitudinal and transverse dispersion, and adsorption in a uniform flow field.

For a two dimensional porous medium in the  $x, y$  plane with mass per unit length  $M$  instantaneously injected along the vertical  $z$  axis, the solution of Eq. (3.23) is given by [33,34]

$$C(x, y, t) = \frac{M}{4\pi n \sqrt{D_x D_y}} \cdot \frac{1}{t} \cdot \exp\left(-\frac{\left(x - \frac{\bar{V}_x t}{R}\right)^2}{\frac{4D_x t}{R}} - \frac{\frac{y^2}{R}}{\frac{4D_y t}{R}}\right) \quad (5.1)$$

### 5.1 Analysis of Standard Solutions of Chloroform in Pentane

Standard solutions of 250 ppb, 500 ppb, 1000 ppb, 1500 ppb, 2000 ppb and 2500 ppb of chloroform in pentane were analysed using a HP 5880A Gas Chromatograph equipped with an auto-sampler, utilizing an Electron Capture Detector. Figure 5.1 shows a sample output from a Gas Chromatograph. Table 5.1 shows the results of the analysis performed. For each sample three runs were performed and the average of the three area counts was used in determining the calibration curve.

To obtain a calibration curve a linear regression model was used. Using the linear regression model, it was found that the standards best fitted a straight line satisfying the following equation, with a  $R^2 = 0.99$

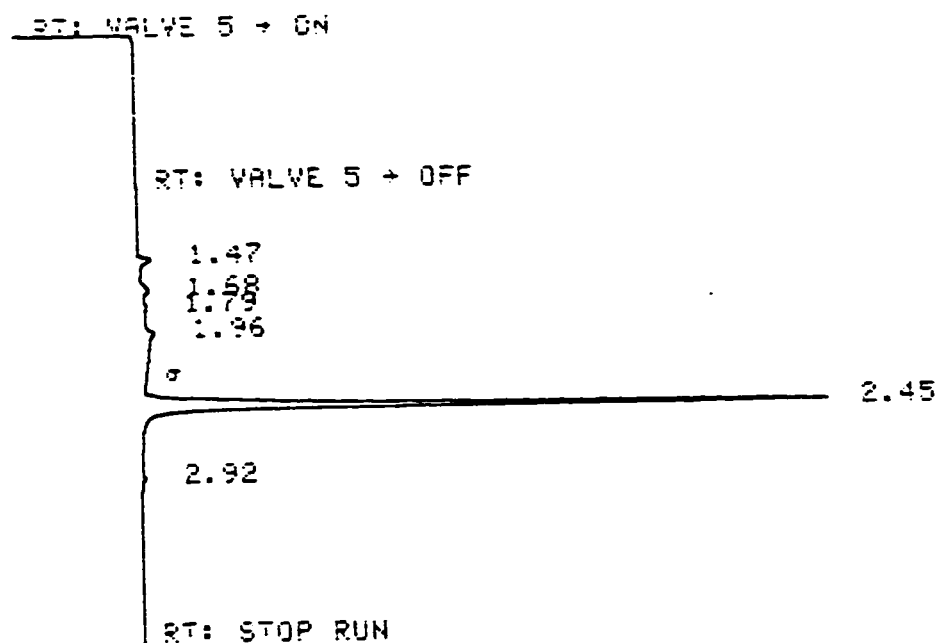
$$Y = 1042.84 + 3.69 X$$

where  $X$  is the concentration of  $\text{CHCl}_3$  in ppb and  $Y$  is the area count.

Rearranging terms,

$$X = 0.27 Y - 282.38$$

Figure 5.2 shows a plot of the concentration of the standards versus the area count. This curve was used to determine the unknown concentration of the samples collected during the experiment.



【hp】 5880A SAMPLER INJECTION @ 20:36 OCT 26, 1987  
 SAMPLE # : ID CODE :  
 17 1000 PPB

AREA %

RT	AREA	TYPE	AREA %
1.47	160.05	SV	2.778
1.68	164.30	VV	2.851
1.79	119.16	VV	2.068
1.96	488.96	VV	8.486
2.45	4802.88	SB	83.353
2.92	26.71	SB	0.464

TOTAL AREA = 5762.06  
 MULTIPLIER = 1

Fig. 5.1. A Sample Output from a Gas Chromatograph

**Table 5.1: Area Count for the Standard Solutions of Chloroform in Pentane analysed using the Gas Chromatograph.**

Concentration of Standards (ppb)	Area Count			
	Run # 1	Run # 2	Run # 3	Average
250	1908.22	1910.63	1911.18	1910
500	2778.71	2858.93	3051.51	2897
1000	4490.52	4700.79	4802.88	4665
1500	6586.90	6949.84	6933.90	6824
2000	7809.99	8736.88	8601.08	8383
2500	9917.92	10283.90	10400.10	10201

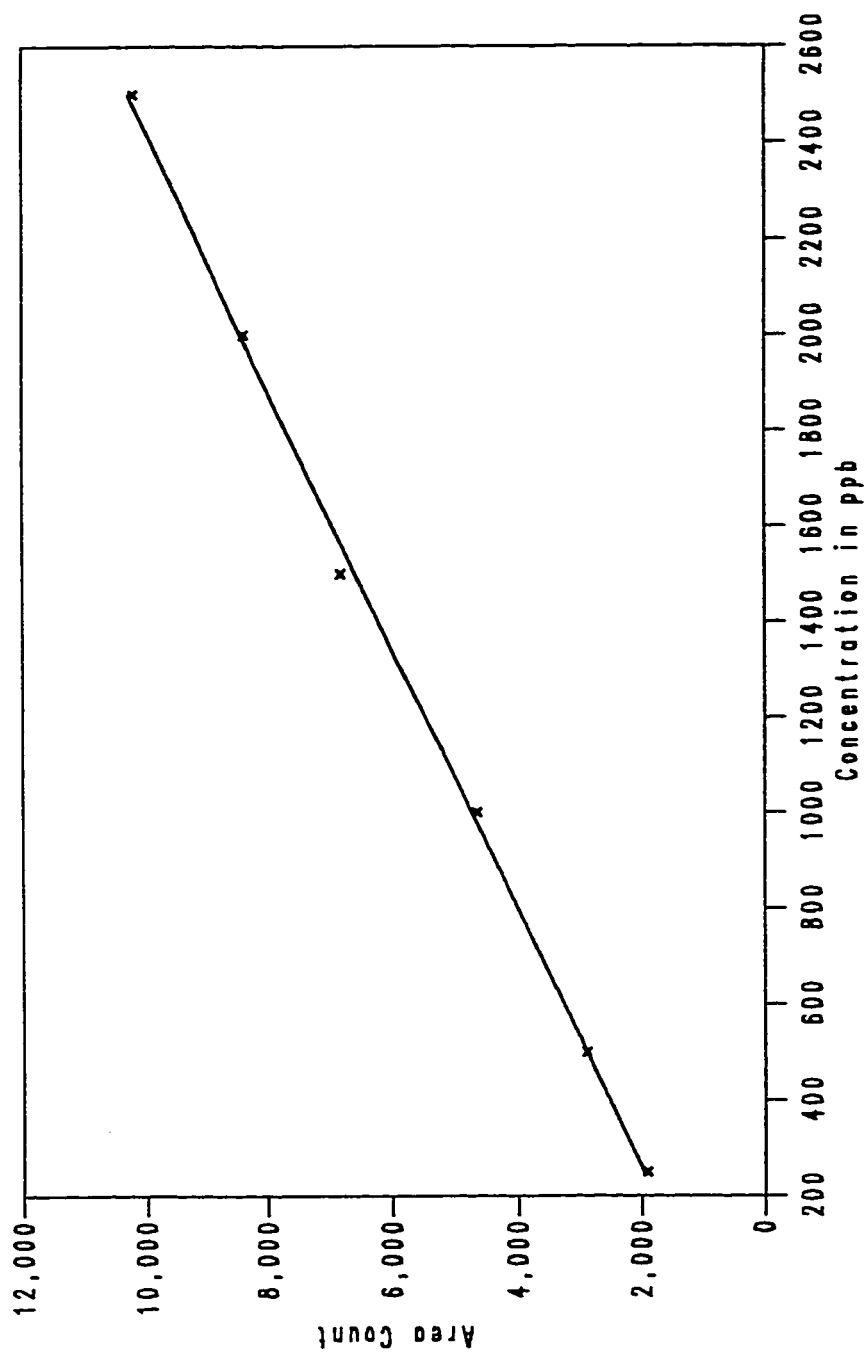


Fig. 5.2. A Standard Calibration Curve for Chloroform in Pentane.

Similarly another set of standard solutions of 250 ppb, 500 ppb, 1000 ppb, 1500 ppb, 2000 ppb, and 2500 ppb of chloroform in pentane were analysed. Table 5.2 shows the results of the analysis performed. For each sample three runs were performed and the average of the three area counts was used in determining the calibration curve.

Using a linear regression model, it was found that the standards best fitted a straight line satisfying the following equation, with a  $R^2 = 0.99$

$$Y = 1146.87 + 4.04 X$$

where  $X$  is the concentration of  $\text{CHCl}_3$  in ppb, and  $Y$  is the area count.

Rearranging terms,

$$X = 0.25 Y - 283.67$$

Figure 5.3 shows a plot of the concentration of the standards versus the area count. This curve was used to determine the unknown concentration of the samples collected during the latter experiments.

## 5.2 Determination of the Longitudinal Dispersion Coefficient $D_x$

A finite slug of chloroform solution was injected at time  $t = 0$ , into the media, and allowed to travel downstream at a known average

**Table 5.2: Area Count for the Standard Solutions of Chloroform in Pentane analysed using the Gas Chromatograph.**

Concentration of Standards (ppb)	Area Count			
	Run # 1	Run # 2	Run # 3	Average
250	2133.38	2139.54	2098.34	2124
500	3109.47	3150.81	3167.73	3143
1000	5000.30	5142.71	5100.33	5081
1500	7415.30	7467.32	7869.16	7584
2000	8914.33	8756.51	9516.21	9062
2500	11003.20	11282.50	11364.20	11217

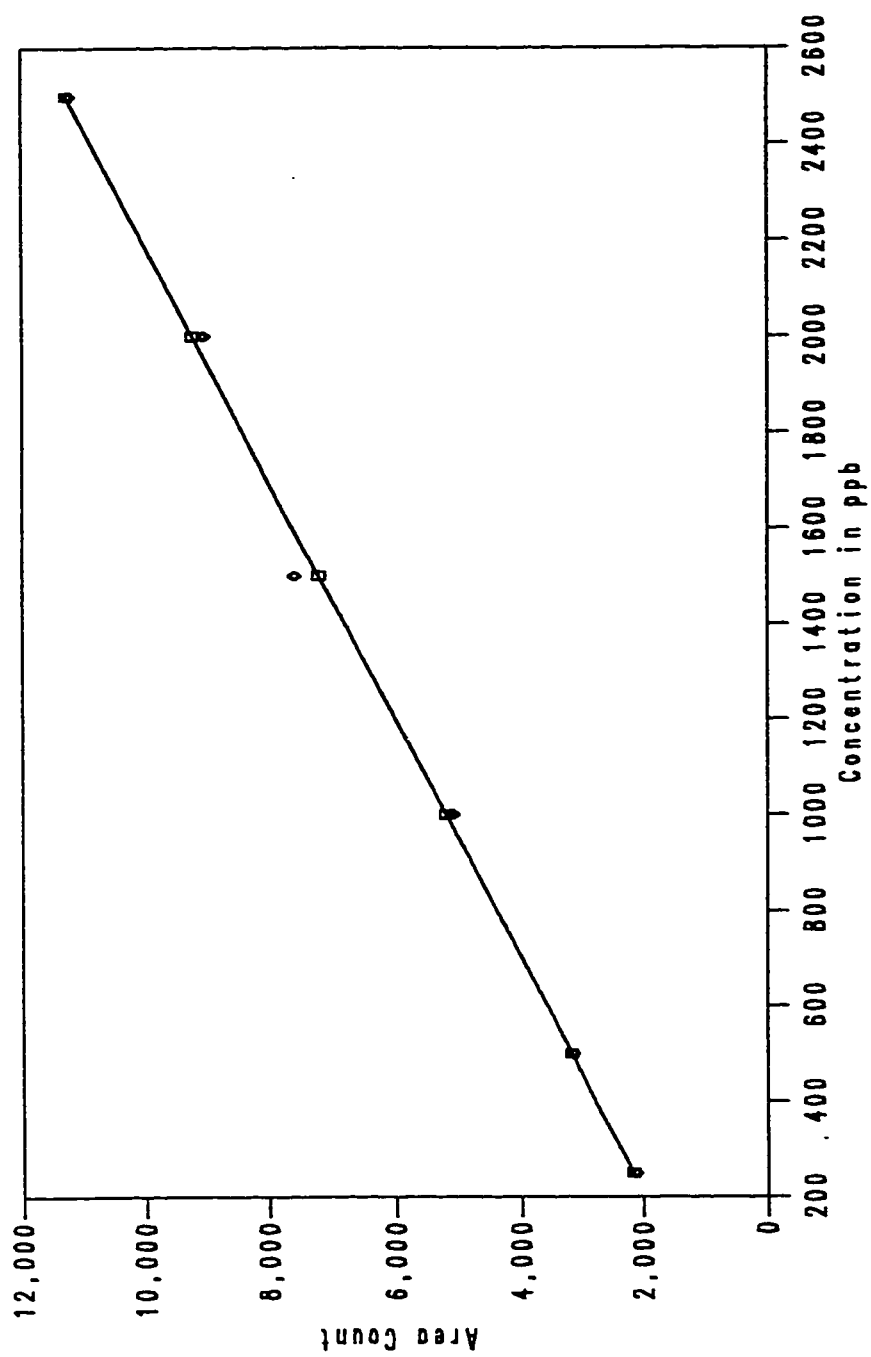


Fig. 5.3. A Standard Calibration Curve For Chloroform in Pentane.



linear velocity,  $\bar{V}_x$  along the direction of flow. At a particular downstream location, samples were withdrawn from the center line of the box (i.e.  $y = 0$ ) and the concentration and time of collection of the samples were recorded.

The location of the sampling port was along the center line, such that  $y = 0$ , and therefore Eq. (5.1) was given by

$$C = \frac{M}{4\pi n \sqrt{D_x D_y}} \cdot \frac{1}{t} \cdot \exp\left[-\frac{\left(x - \frac{\bar{V}_x t}{R}\right)^2}{\frac{4D_x t}{R}}\right] \quad (5.2)$$

or

$$Ct = \frac{M}{4\pi n \sqrt{D_x D_y}} \exp\left[-\frac{\left(x - \frac{\bar{V}_x t}{R}\right)^2}{\frac{4D_x t}{R}}\right] \quad (5.3)$$

Taking logs of both sides yields

$$\ln Ct = \ln\left(\frac{M}{4\pi n \sqrt{D_x D_y}}\right) - \frac{\left(x - \frac{\bar{V}_x t}{R}\right)^2}{\frac{4D_x t}{R}} \quad (5.4)$$

Rearranging terms

$$\ln Ct = -\frac{\left(x - \frac{\bar{V}_x t}{R}\right)^2}{\frac{4D_x t}{R}} + \ln \frac{M}{4\pi n \sqrt{D_x D_y}} \quad (5.5)$$

For any given experiment,

the term  $\frac{M}{4\pi n\sqrt{D_x D_y}}$  is a constant.

Therefore Eq. (5.5) can be written as

$$\ln Ct = -\frac{1}{D_x} \frac{\left(x - \frac{\bar{V}_x t}{R}\right)^2}{\frac{4t}{R}} + K_1 \quad (5.6)$$

From the experimental measurements of C and t, the term  $\ln Ct$

could be determined. A plot of  $\frac{\left(x - \frac{\bar{V}_x t}{R}\right)^2}{\frac{4t}{R}}$  versus  $\ln Ct$  yields a

straight line whose resulting slope is given by  $\frac{-1}{D_x}$  and an intercept

equal to  $K_1$ . The only unknown in the term  $\frac{\left(x - \frac{\bar{V}_x t}{R}\right)^2}{\frac{4t}{R}}$  is R, the

retardation factor given by,

$$R = \left(1 + \frac{\rho_b}{n} K_d\right) \quad (5.7)$$

where the bulk density  $\rho_b = 2.64 \text{ g/cm}^3$ , and porosity  $n = 0.36$  are constants. The distribution coefficient  $K_d$  can be obtained from a plot of the mass of solute adsorbed per unit dry mass of soil ( $\mu\text{g/g}$ ) versus the concentration in the aqueous phase ( $\mu\text{g/ml}$ ).

### 5.2.1 Determination of the Distribution Coefficient $K_d$ for Chloroform

The distribution coefficient  $K_d$  can be obtained from a plot of the mass of solute adsorbed per unit dry mass of soil ( $\mu\text{g/g}$ ) versus the concentration in the aqueous phase ( $\mu\text{g/ml}$ ). Experiments were conducted to determine the distribution coefficient as mentioned in Chapter 4. The data obtained from the experiments are shown in Table 5.3. It can be observed from the data, that there was a reduction in the effluent concentration for each experiment. This can be attributed to the fact that adsorption has taken place. Furthermore, as the influent concentration of each experiment was increased, there was a corresponding increase in the effluent concentration.

To determine the mass of solute adsorbed per unit dry mass of the soil, the influent mass of chloroform, and the effluent mass of chloroform had to be determined for all three runs. A sample calculation is shown below.

Volume of chloroform solution used in the column experiment = 23 ml.

Weight of medium used in the column experiment = 92.7 g.

i.e. if 100 g of the medium was packed in the column then the volume of chloroform solution required would be =  $\frac{23}{92.7} (100) = 24.8$  ml.

Concentration of chloroform solution used in experiment #1 = C

**Table 5.3: Influent and Effluent Concentrations of the Chloroform Solution Injected for the determination of  $K_d$  for Chloroform.**

Run #	Influent Area Count	Influent Concentration x1000 ppb	Effluent Area Count	Effluent Concentration x1000 ppb
1	1448.58	110.18	1078.50	9.89
2	1842.86	217.03	1156.13	30.93
3	2239.24	324.45	1230.78	51.16

$$= 110.18 \times 1000 \mu\text{g}/1000 \text{ ml} = 110.18 \mu\text{g}/\text{ml}$$

i.e. 1 ml of chloroform solution contained 110.18  $\mu\text{g}$ . Therefore  
 24.8 ml of chloroform solution contained =  $110.18 \times 24.8 =$   
 2732.46  $\mu\text{g}$ .

Mass of chloroform at influent = 2732.46  $\mu\text{g}/100 \text{ g medium}$

Mass of chloroform at effluent =  $9.89 \times 24.8 = 245.27$   
 $\mu\text{g}/100 \text{ g medium}$

Mass of chloroform adsorbed = S

$$= 2732.46 - 245.27$$

$$= 2487.19 \mu\text{g}/100 \text{ g medium}$$

$$= 24.87 \mu\text{g}/\text{g medium}$$

Table 5.4 shows the mass of solute adsorbed per unit dry mass of soil ( $\mu\text{g}/\text{g}$ ) along with the corresponding influent concentrations ( $\mu\text{g}/\text{ml}$ ).

Figure 5.4 shows a plot of the mass of solute adsorbed per unit dry mass of soil ( $\mu\text{g}/\text{g}$ ) versus influent concentration ( $\mu\text{g}/\text{ml}$ ). A linear regression of the data was performed, and a  $R^2 = 0.99$  was obtained. The  $K_d$  value was obtained from the slope of the resulting curve, i.e.  $K_d = 0.20 \text{ ml}/\text{g}$ .

### 5.3 Slug Input Experiments

A finite slug of a known concentration of chloroform solution was injected into the media at time  $t = 0$ , and allowed to travel down-

**Table 5.4: Mass of Solute Adsorbed per Unit Dry Mass of Soil for the corresponding Influent Concentrations.**

Run #	Mass of Solute Absorbed Per Unit Dry Mass of Soil ( $\mu\text{g/g}$ )	Influent Concentration ( $\mu\text{g/ml}$ )
1	24.87	110.18
2	46.15	217.03
3	67.78	324.45

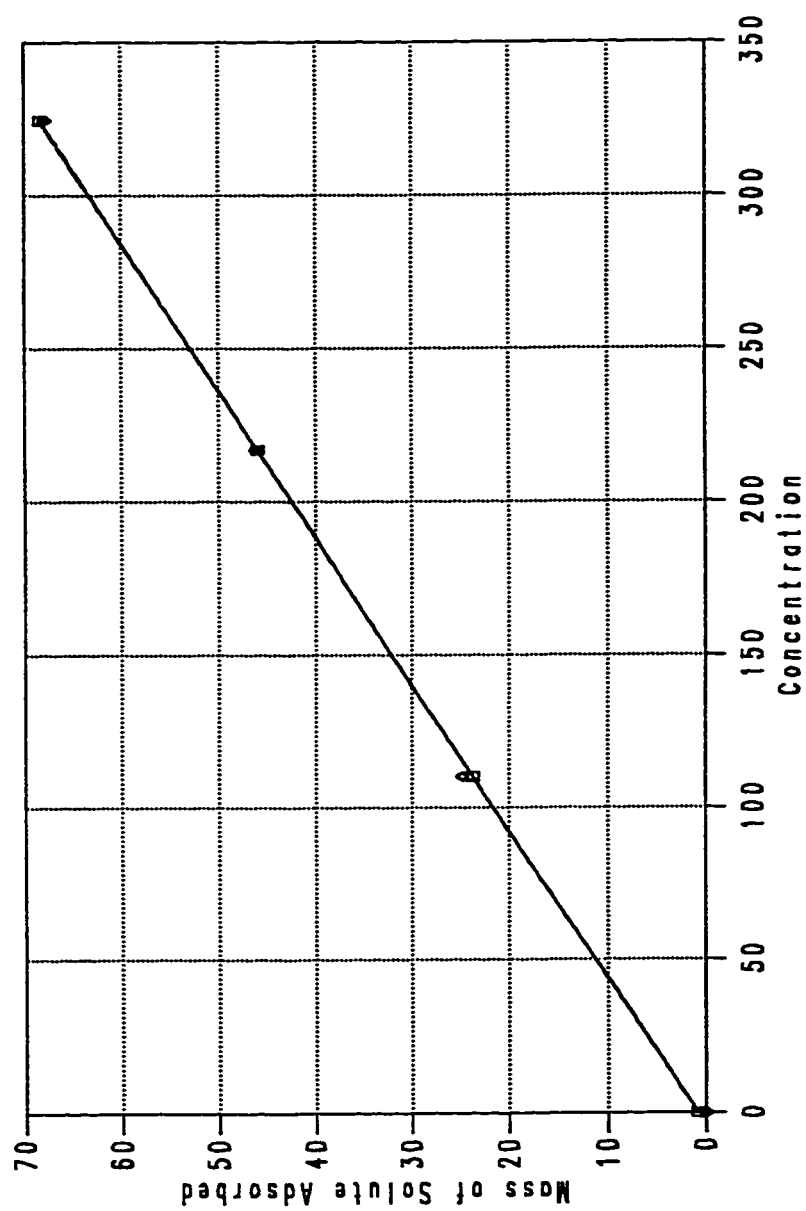


Fig. 5.4. Mass of Solute Adsorbed Per Unit Dry Mass of Soil ( $\mu\text{g/g}$ ) Versus Concentration in the Aqueous Phase ( $\mu\text{g/ml}$ ).

stream at a known average linear velocity,  $\bar{V}_x$  along the direction of flow. Sampling was carried out at a port along the center line of the box.

Table 5.5 shows the discharge at the outlet of the outflow constant head tank, the specific discharge, and the hydraulic conductivity of the medium.

### 5.3.1 Results of a Typical Slug Input Experiment

For each experiment two data sheets were prepared. Data sheets 1 to 20 show the results of the experiments conducted and are provided in the Appendix. As mentioned above the experiments were conducted, and the samples were collected, preserved when necessary, and analysed using the GC. The area count of the unknown samples were obtained from the chromatogram, and the corresponding concentrations were determined from the calibration curve.

Table 5.6 shows the time of collection of the sample, the area count obtained, and the corresponding concentration of  $\text{CHCl}_3$  in ppb. Table 5.7 shows the reduced form of the data to facilitate the

plotting of  $\frac{(\bar{V}_x t - \frac{x}{R})^2}{\frac{4t}{R}}$  vs.  $\ln C_t$ .

Figure 5.5 to Figure 5.14 shows the plot of  $\frac{(\bar{V}_x t - \frac{x}{R})^2}{\frac{4t}{R}}$  versus



**Table 5.5: Discharge at the Outlet of the Outflow Constant Head Tank, and the corresponding Hydraulic Conductivities.**

Experiment No.	Q (cm <sup>3</sup> /sec)	V(cm/sec)	h <sub>2</sub> - h <sub>1</sub> (cm)	K(cm/sec)
1	33.33	0.0185	8.25	0.478
2	37.04	0.0205	9.21	0.475
3	32.05	0.0178	7.30	0.520
4	21.79	0.0121	4.28	0.602
5	30.30	0.0168	6.67	0.537
6	30.30	0.0168	6.67	0.537
7	30.30	0.0168	6.67	0.537
8	30.30	0.0168	6.67	0.537
9	30.30	0.0168	6.67	0.537
10	25.06	0.0139	4.60	0.644
11	24.15	0.0134	4.29	0.667

**Table 5.6:** Experimental data showing the Time of Collection of the Sample, the Area Count, and the corresponding Concentration of  $\text{CHCl}_3$  in ppb.

Time (min)	Sample #	Area Count	Conc. of $\text{CHCl}_3$ in ppb
0	1	840	0
30	2	852	0
60	3	1161	32
90	4	1793	203
120	5	2369	359
150	6	2417	372
190	7	1852	219
210	8	1648	164
250	9	1656	166
270	10	1202	43
300	11	1124	22

Table 5.7: Reduced form of the data to facilitate the plotting of

$$\frac{\left(x - \frac{\bar{V}_x t}{R}\right)^2}{\frac{4t}{R}} \text{ vs. } \ln Ct.$$

t (secs)	C ( $\mu\text{g}/\text{cm}^3$ )	$\left(x - \frac{\bar{V}_x t}{R}\right)$ (cm)	$\frac{\left(x - \frac{\bar{V}_x t}{R}\right)^2}{\frac{4t}{R}}$ ( $\text{cm}^2/\text{sec}$ )	$\ln Ct$
0	0.0	-	-	-
1800	0.0	-	-	-
3600	0.032	85.20	1.2381	4.747
5400	0.203	47.75	0.2593	7.000
7200	0.359	10.30	0.0090	7.857
9000	0.372	-27.16	0.0503	8.116
11400	0.219	-77.09	0.3201	7.823
12600	0.164	-102.06	0.5076	7.634
15000	0.064	-151.99	0.9456	6.867
16200	0.043	-176.96	1.1869	6.546
18000	0.022	-214.41	1.5681	5.981

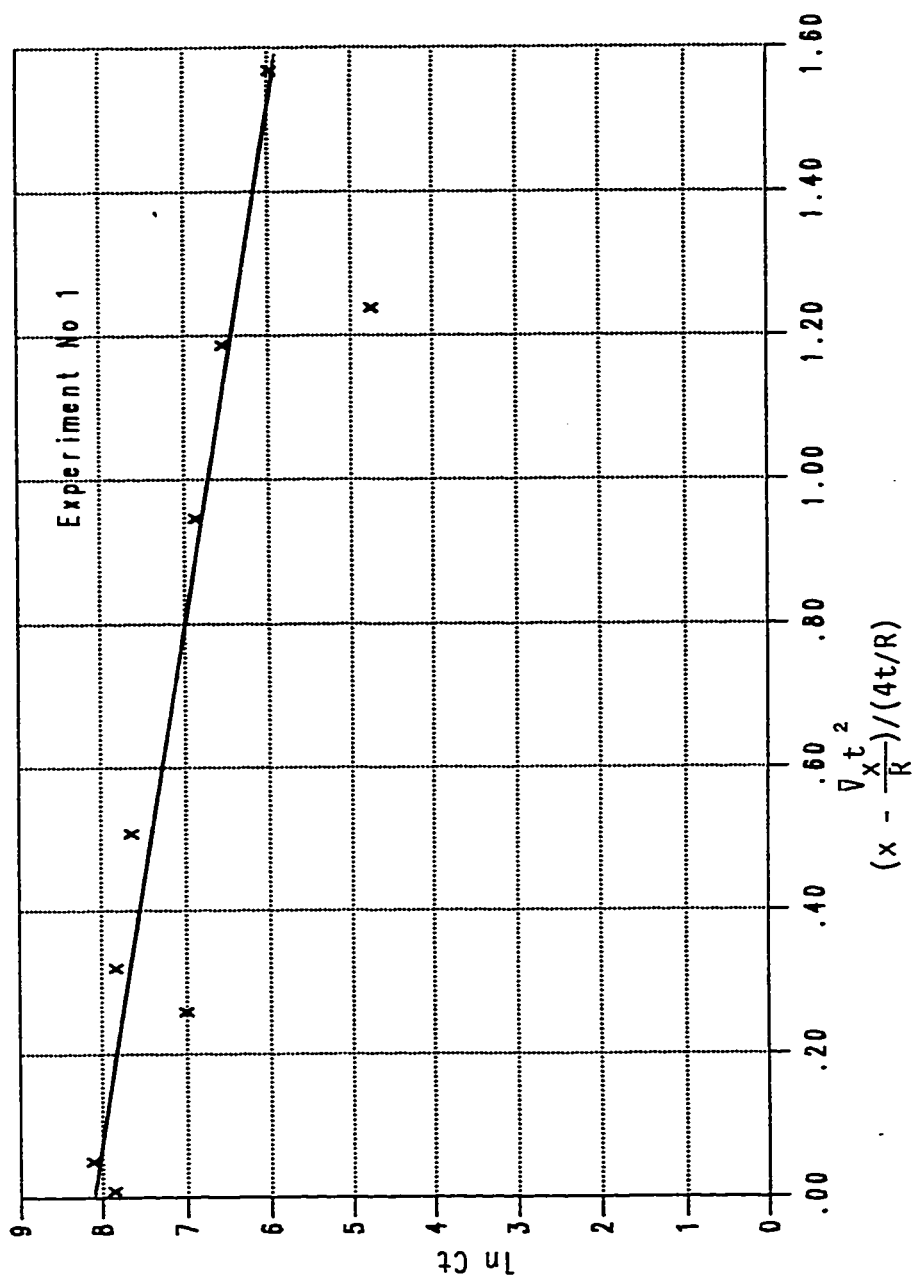


Fig. 5.5. A Plot of  $(x - \frac{x}{R}) / (4t/R)$  Versus  $\ln Ct$ .

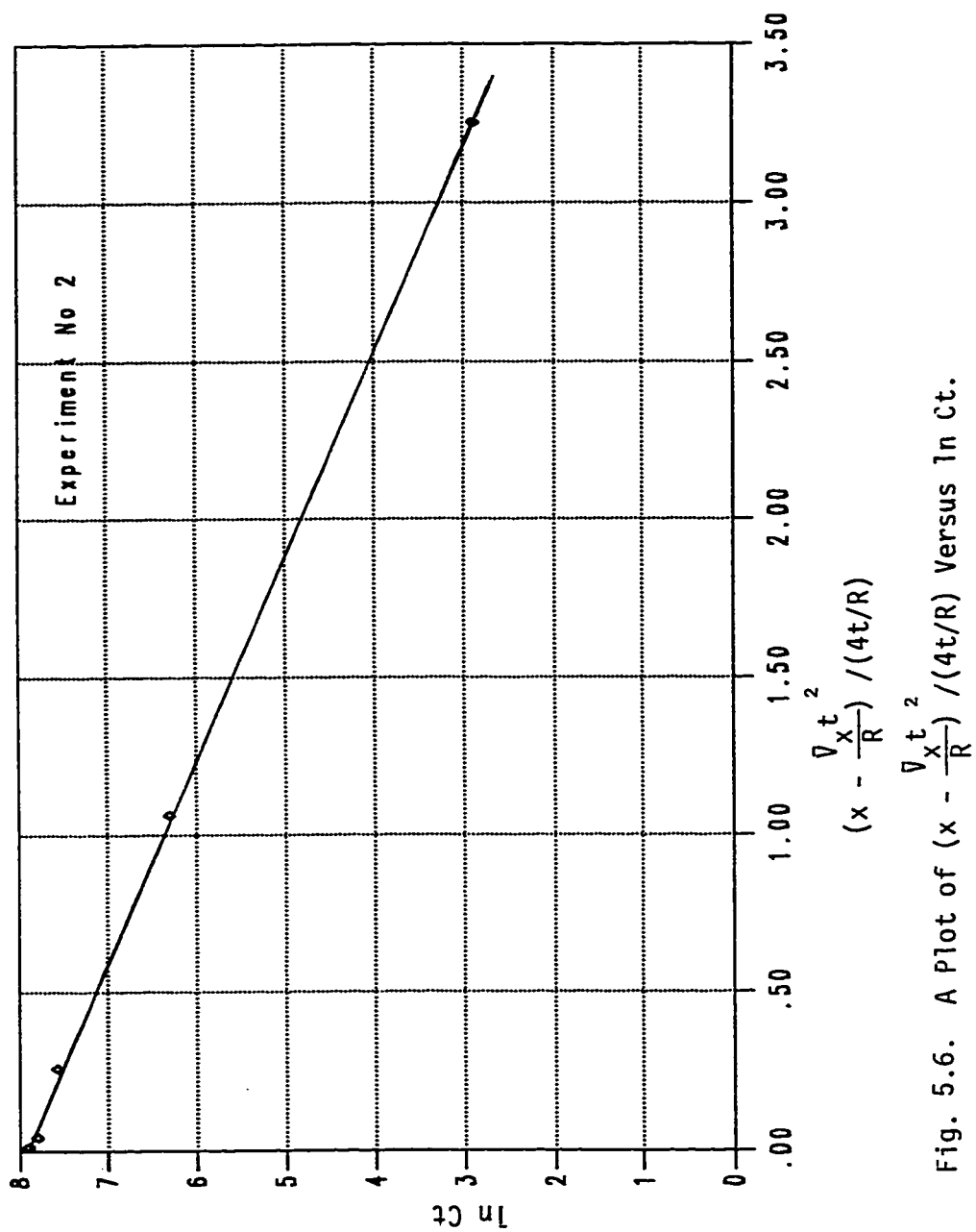


Fig. 5.6. A Plot of  $(x - \frac{x}{R}) / (4t/R)$  Versus  $\ln C_t$ .

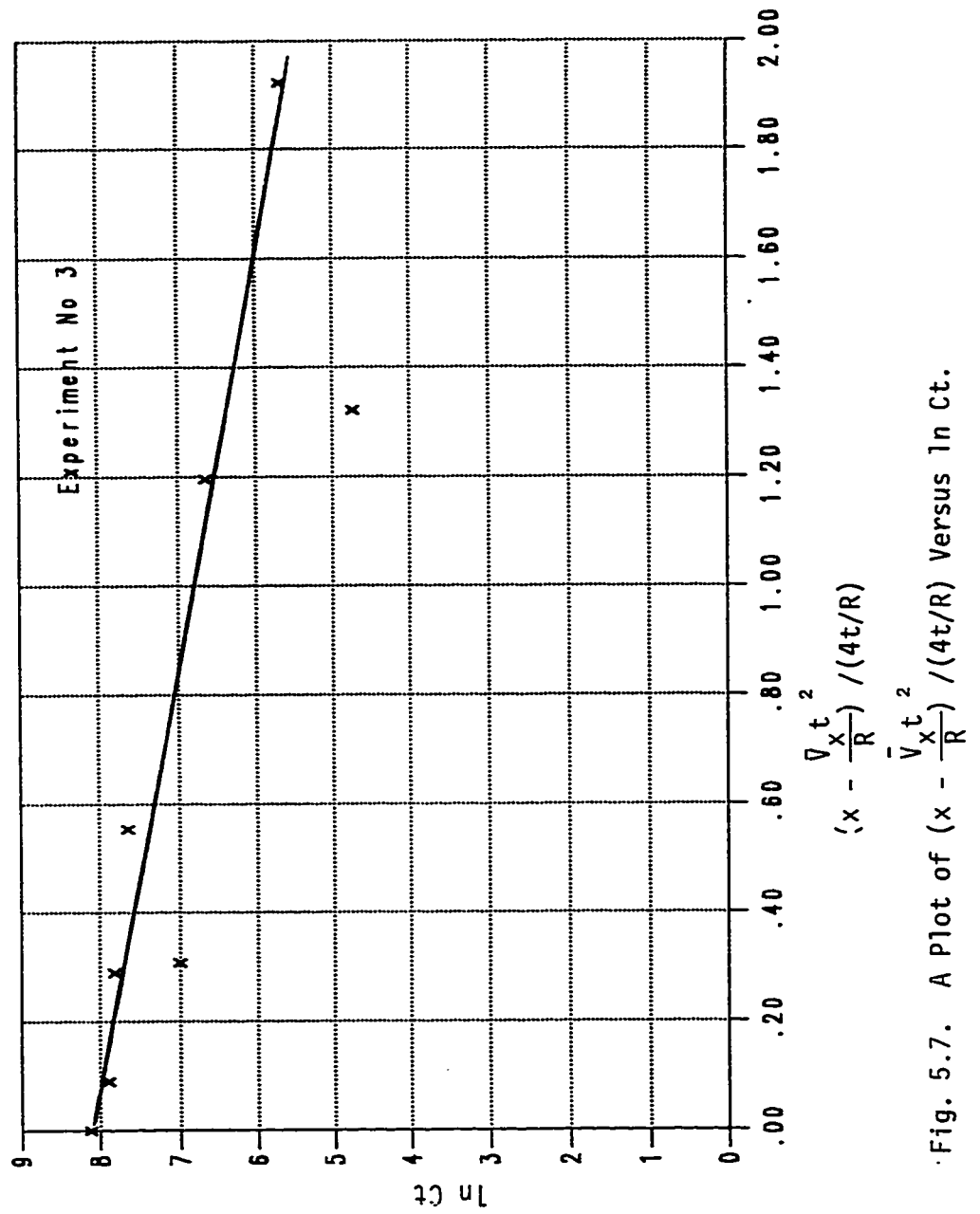


Fig. 5.7. A Plot of  $(x - \frac{x}{R}) \frac{t^2}{4t/R}$  Versus  $\ln C_t$ .

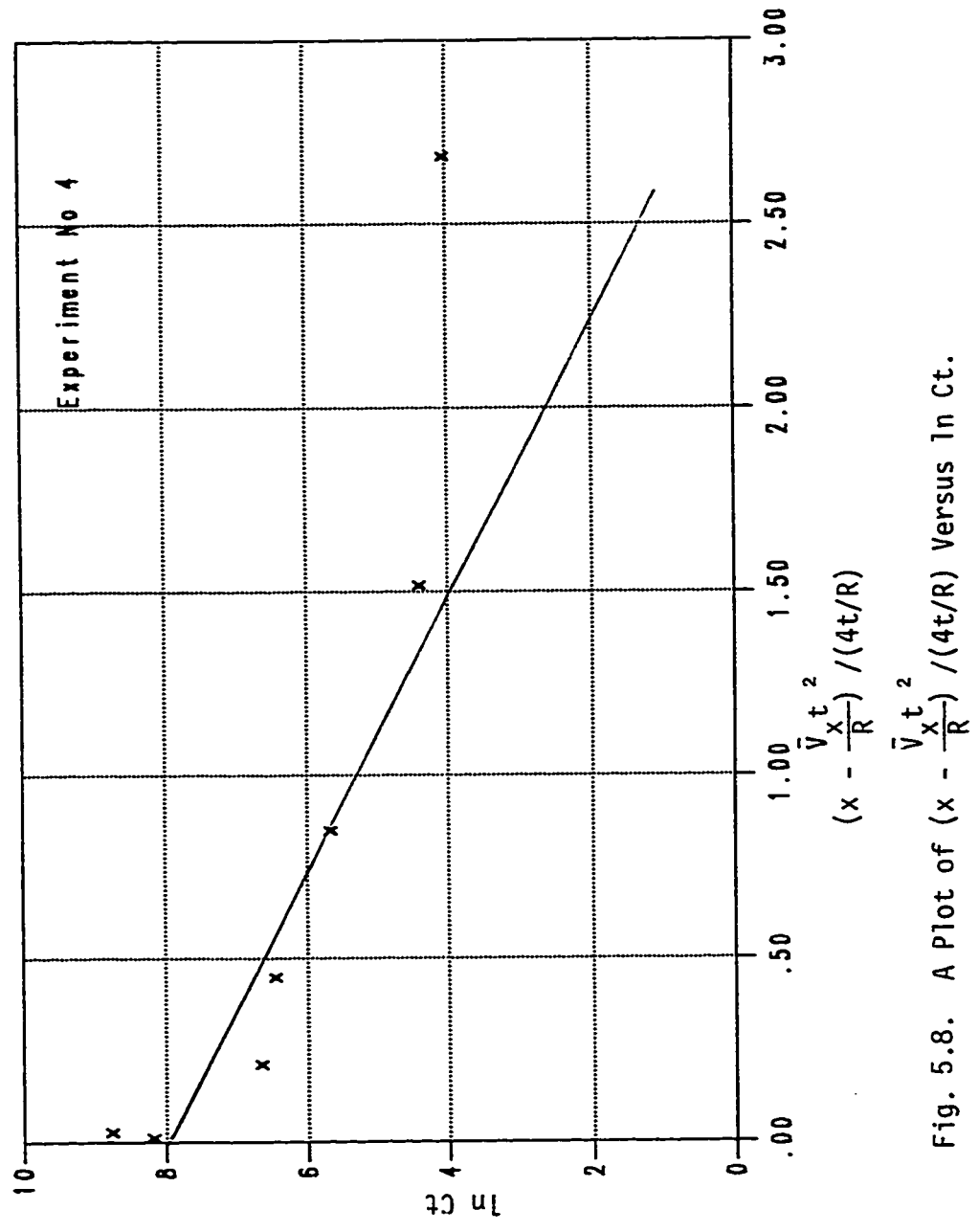


Fig. 5.8. A Plot of  $(x - \frac{\bar{x}}{R}) \frac{t^2}{(4t/R)}$  Versus  $\ln Ct$ .

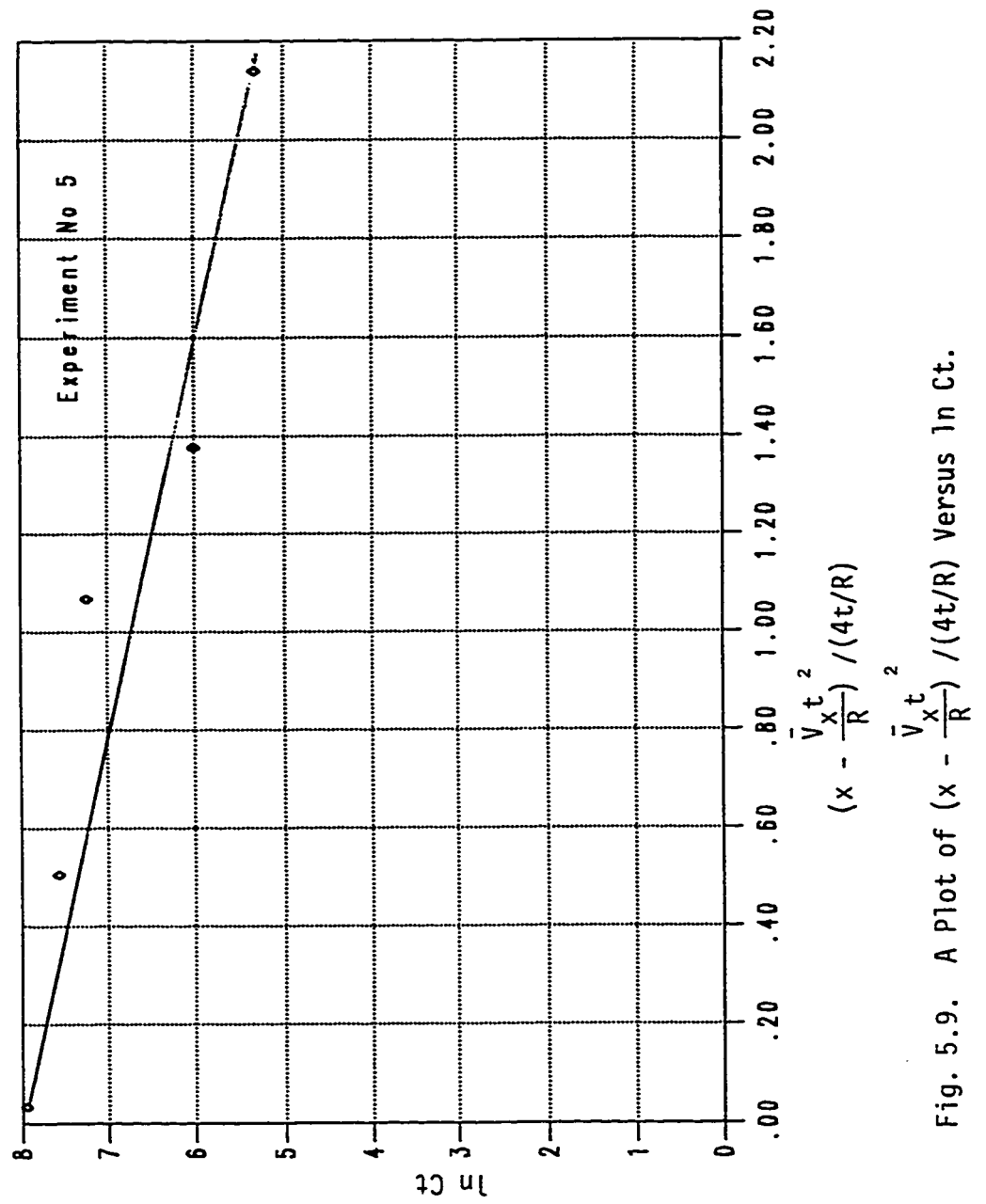


Fig. 5.9. A Plot of  $(x - \frac{x}{R}) / (4t/R)$  Versus  $\ln Ct$ .



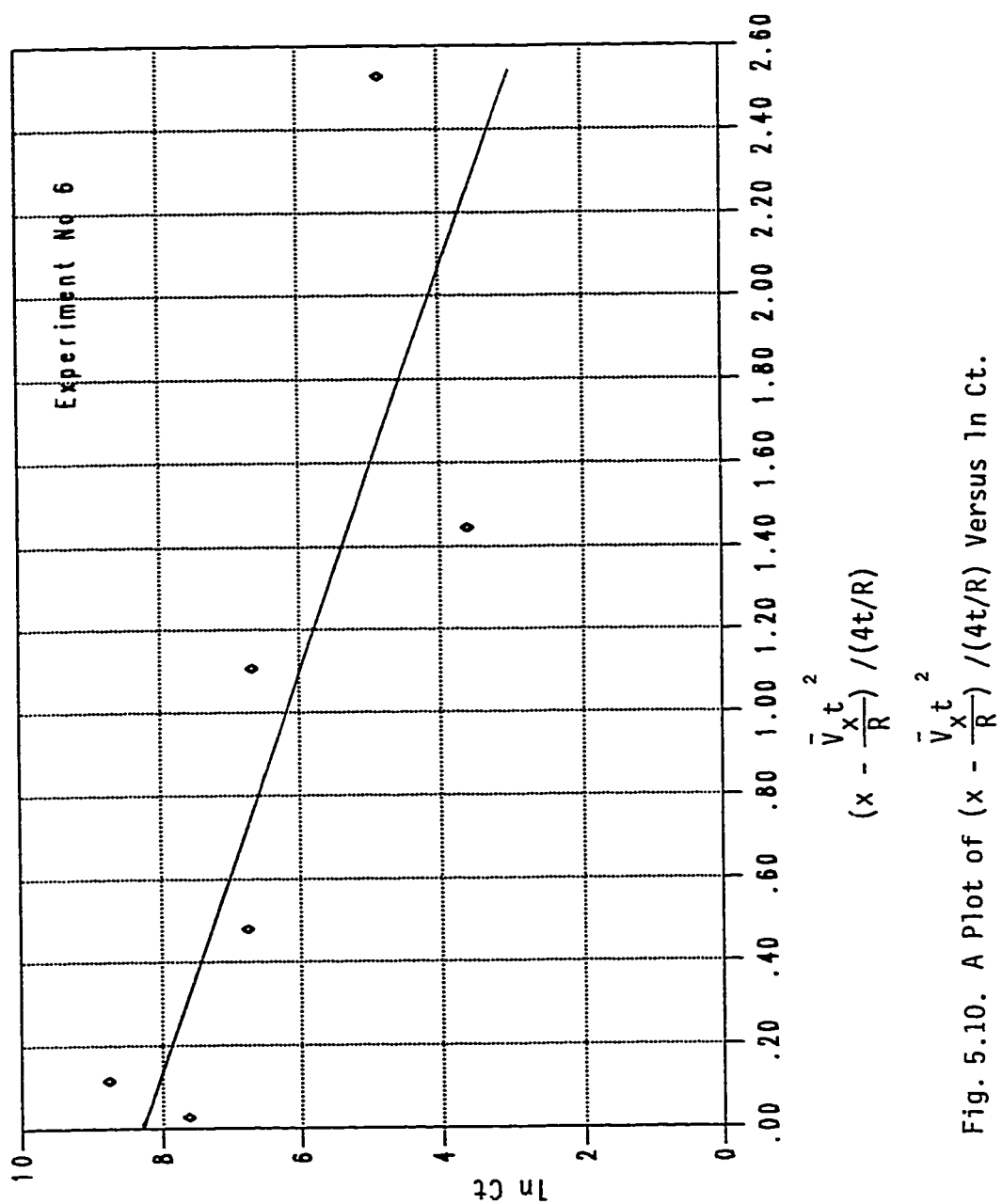


Fig. 5.10. A Plot of  $\left(x - \frac{x_t}{R}\right)^2 / (4t/R)$  Versus  $\ln C_t$ .

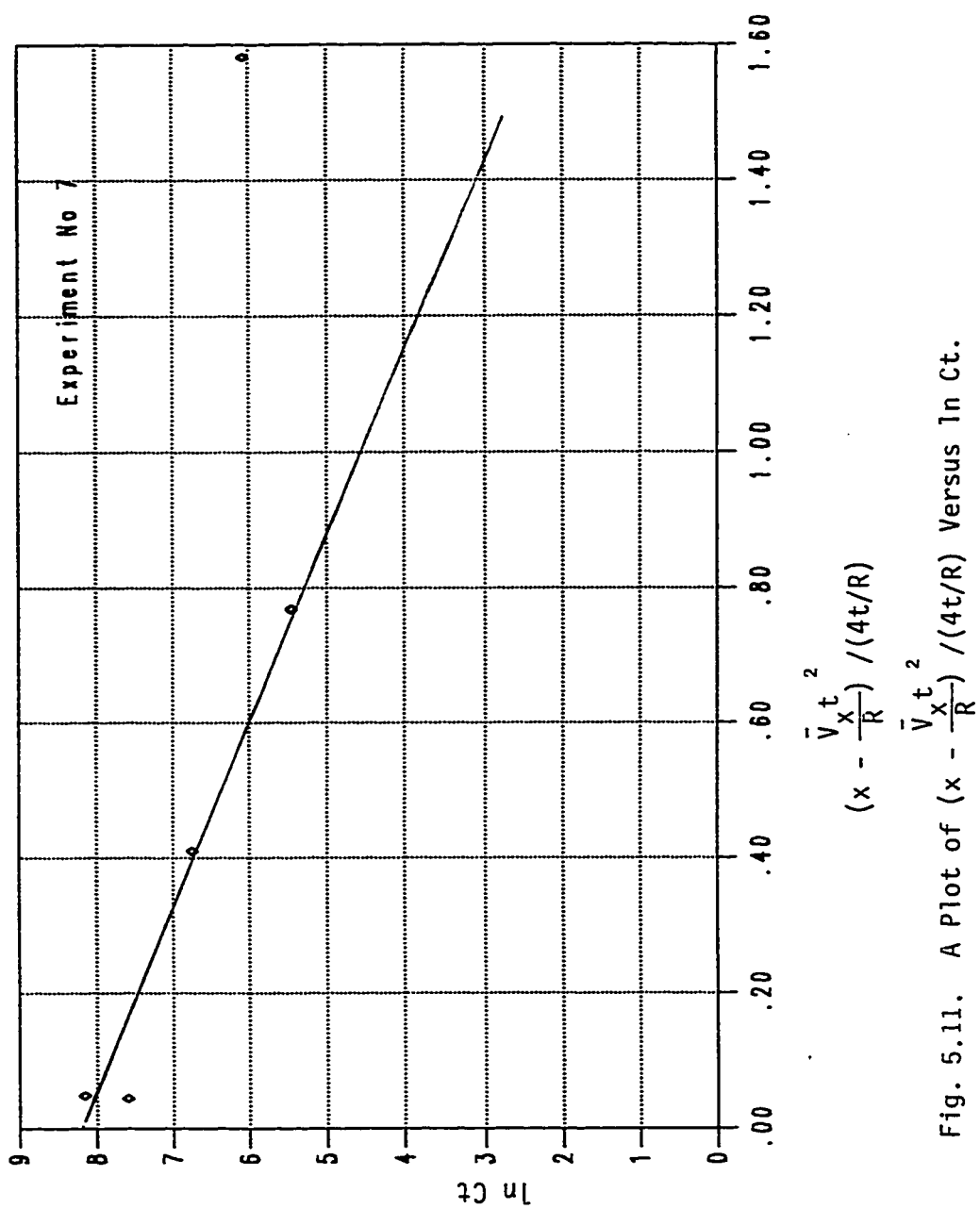


Fig. 5.11. A Plot of  $\left( x - \frac{x}{R} \right) / (4t/R)$  Versus  $\ln Ct$ .

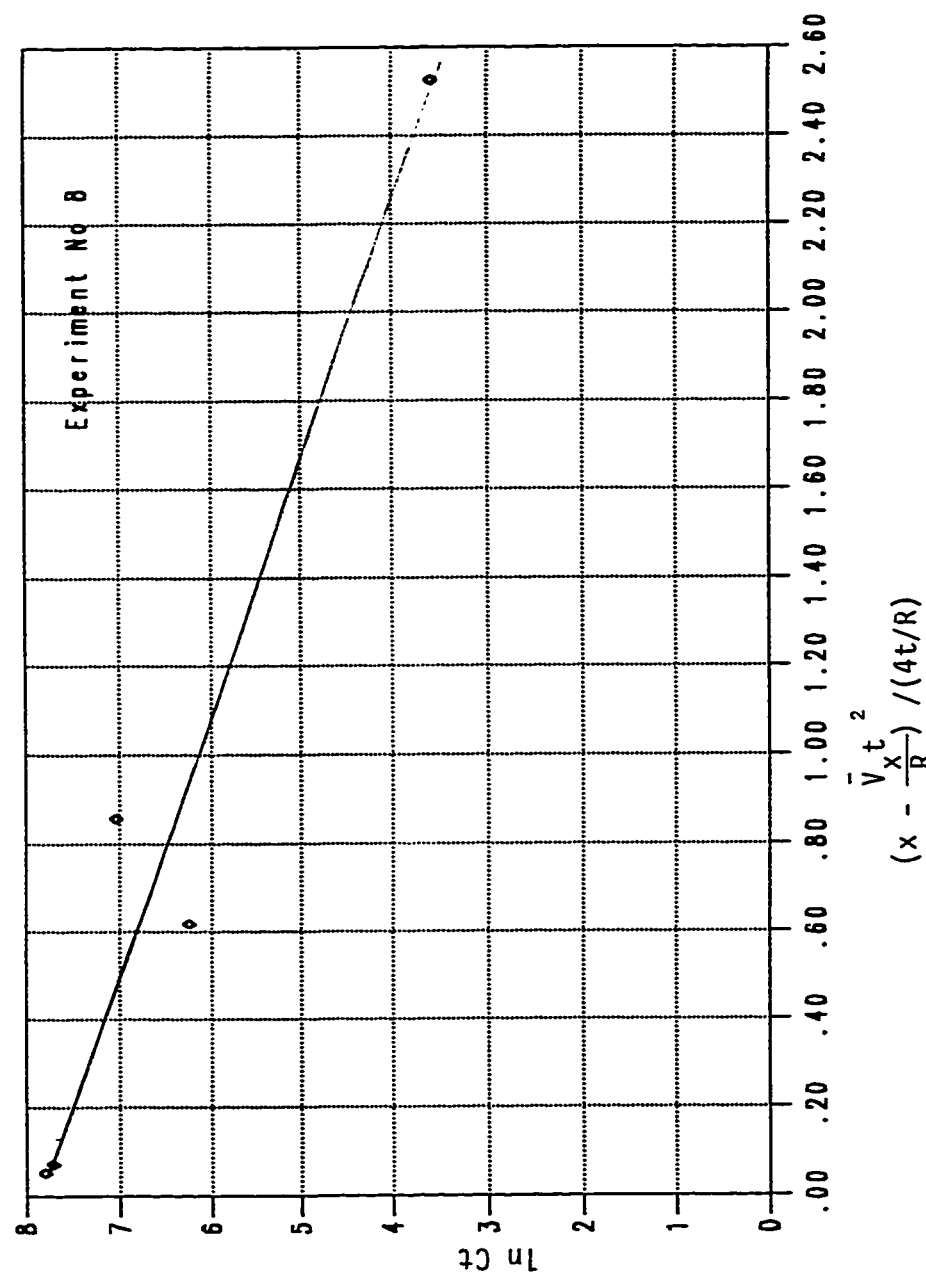


Fig. 5.12. A Plot of  $\left( x - \frac{x}{R} \right) / (4t/R)$  Versus  $\ln Ct$ .

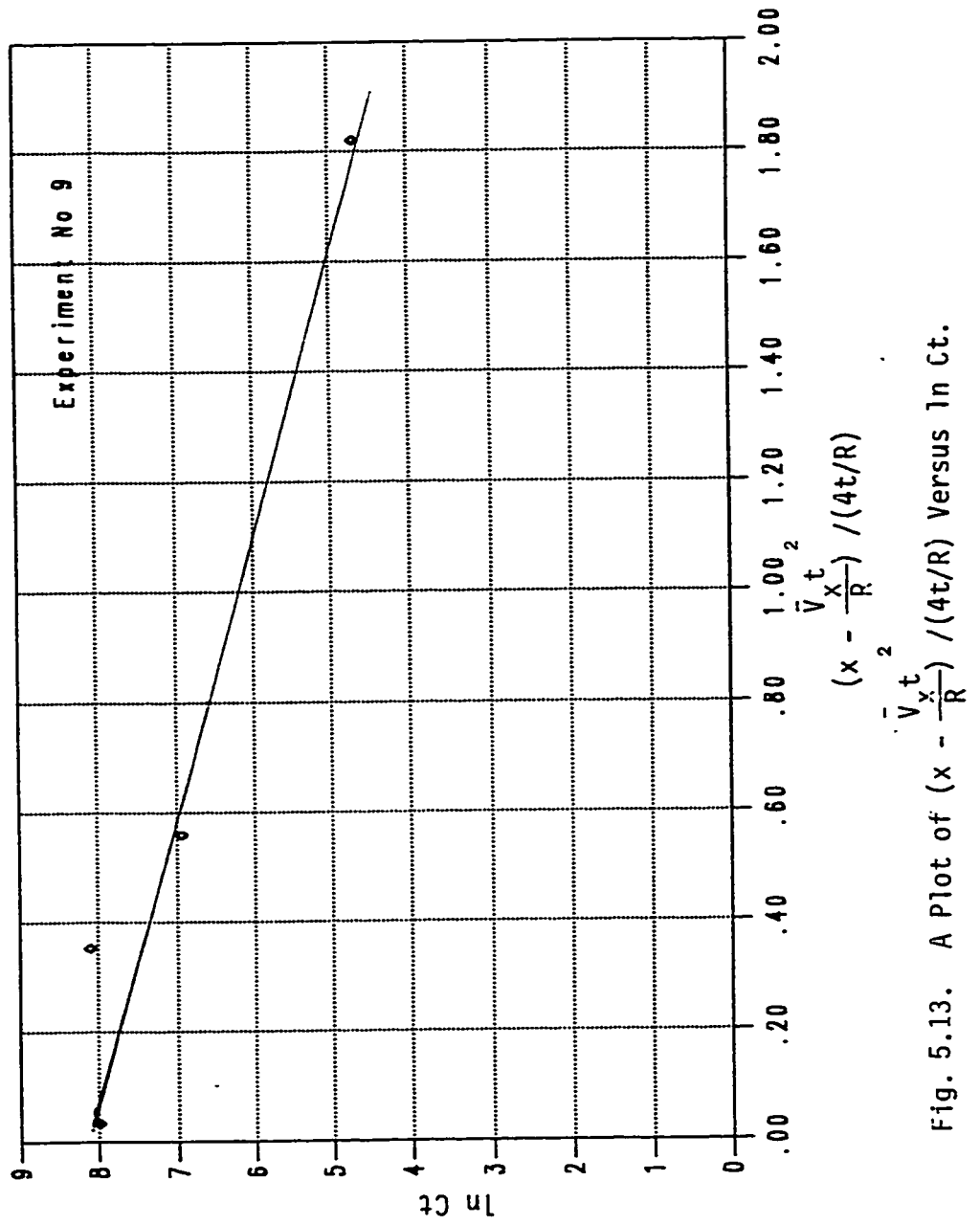


Fig. 5.13. A Plot of  $(x - \frac{V_x t}{R}) / (4t/R)$  Versus  $\ln Ct$ .

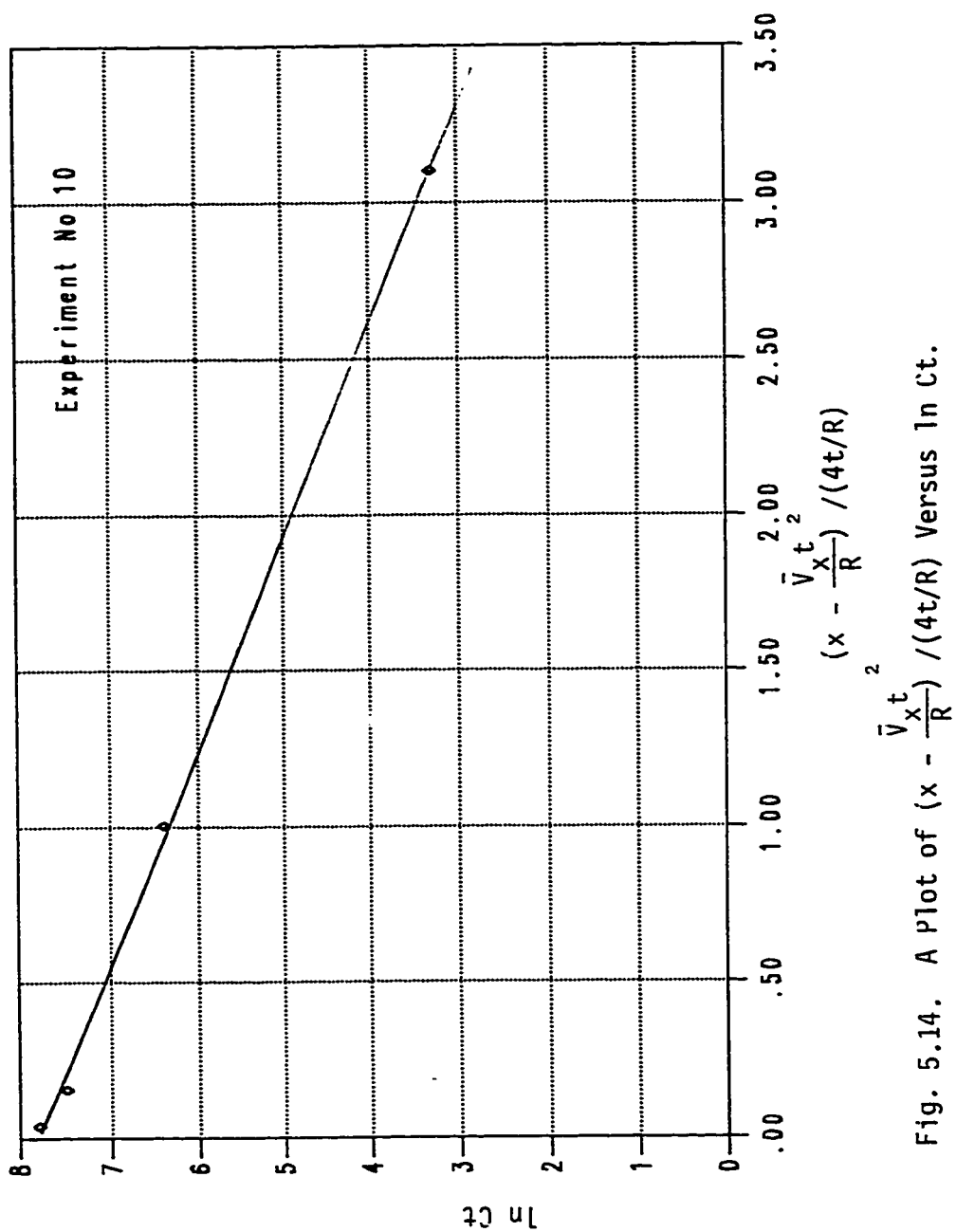


Fig. 5.14. A Plot of  $(x - \frac{x_t}{R}) / (4t/R)$  Versus  $\ln Ct$ .

In Ct. Using the linear regression model a straight line that best fitted the experimental data was obtained. The negative reciprocal of the slope was used to calculate the longitudinal dispersion coefficient,  $D_x$ . A sample calculation is provided below.

For Experiment #1

From Figure 5.5

The slope of the straight line = -1.575.

$$\text{Longitudinal dispersion coefficient} = \frac{1}{1.575} = 0.635 \text{ cm}^2/\text{sec}.$$

Table 5.8 shows the average linear velocity along with the calculated longitudinal dispersion coefficients. Figure 5.15 shows a plot of the average linear velocity versus the longitudinal dispersion coefficient. Using a linear regression model the data best fitted a straight line, resulting in a slope which is equivalent to the longitudinal dispersivity,  $\alpha_x = 0.195 \text{ cm}$ .

Bear [64], Freeze and Cherry [66], Anderson [41] and others reported that the magnitude of the dispersivity changes, depending on the scale at which the measurements were taken. According to these authors, dispersivity values obtained from column tests on disturbed or undisturbed samples of unconsolidated geological materials invariably yield values in the range 0.01 cm to 1 cm.

From Figure 5.15 it can be stated that there was no significant change in the longitudinal dispersion coefficient when the average

**Table 5.8: Longitudinal and Transverse Dispersion Coefficients.**

Slope	Intercept	Average Linear Velocity $\bar{V}_x$ (cm/sec)	Longitudinal Dispersion Coefficient $D_x$ (cm <sup>2</sup> /sec)	Lateral Dispersion Coefficient $D_y$ (cm <sup>2</sup> /sec)
1.575	8.017	0.0511	0.635	0.50018
1.543	7.922	0.0566	0.648	0.00020
1.489	8.000	0.0492	0.671	0.00015
1.619	8.021	0.0334	0.618	0.00021
1.567	8.126	0.0464	0.638	0.00018
1.451	7.805	0.0384	0.689	0.00015

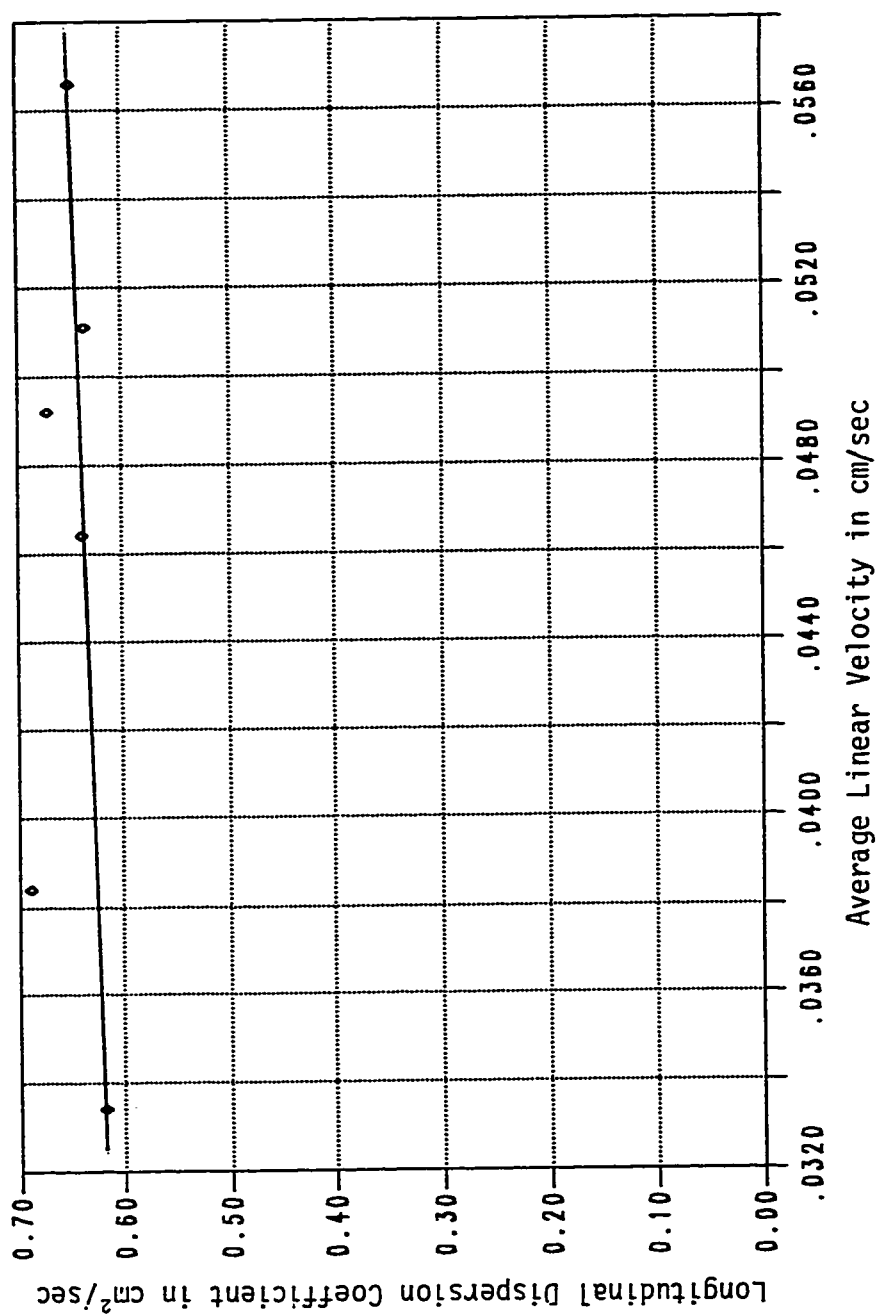


Fig. 5.15. Variation of the Longitudinal Dispersion Coefficient in cm²/sec With the Average Linear Velocity in cm/sec.



groundwater velocity was varied.

### 5.3.2 Breakthrough Curves

The concentration versus time relation, known as a breakthrough curve, resulting from a typical slug input experiment is shown in Figure 5.16. Samples were collected from a port located 160.1 cm away from the source. During the first 40 min there was no evidence of any chloroform present at this location. With time it can be seen that the chloroform has moved into this location. Also, the bulk of the plume arrived after about 135 min. Once the plume has moved away, the tailing effect, i.e. a gradual drop in the concentration with time was observed. Similarly Figure 5.17 to Figure 5.24 shows the breakthrough curve resulting from the other experiments. From these breakthrough curves the development of the plume and the attenuation effect with respect to time was clearly observed.

Figure 5.25 shows a plot of the concentration variation along the direction of flow at various time intervals, and Figure 5.26 shows a plot of the concentration variation with time for samples collected along the direction of flow. It can be observed that the bulk of the plume arrived at the port closest to the source within the first 30 min. With time there was a drop in the concentration level at the first port. At the second port, the concentration increased from  $0.021 \mu\text{g}/\text{cm}^3$  to  $0.884 \mu\text{g}/\text{cm}^3$  during the first 120 min and then gradually dropped with time. Similarly at the third port, the

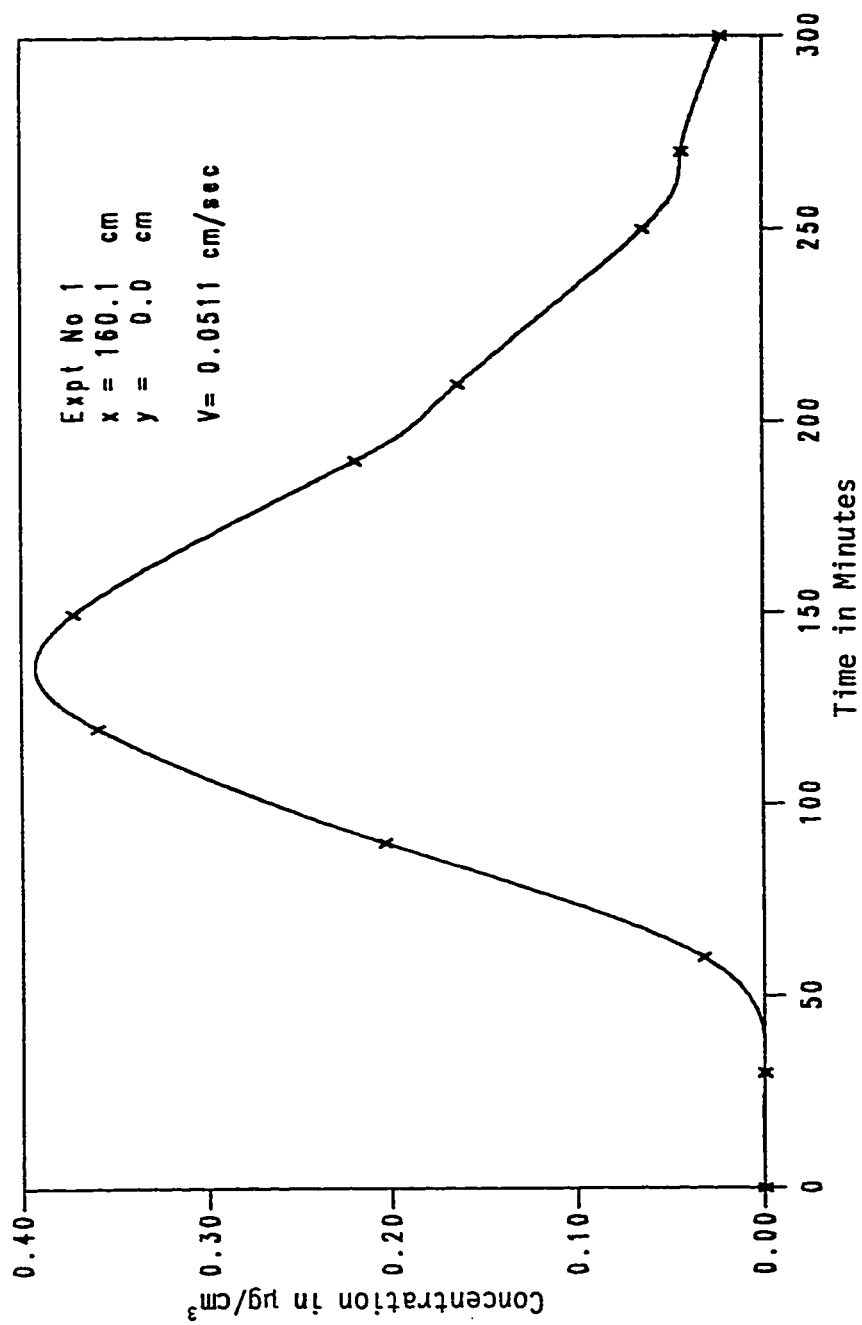


Fig. 5.16. Concentration Variation With Respect to Time.

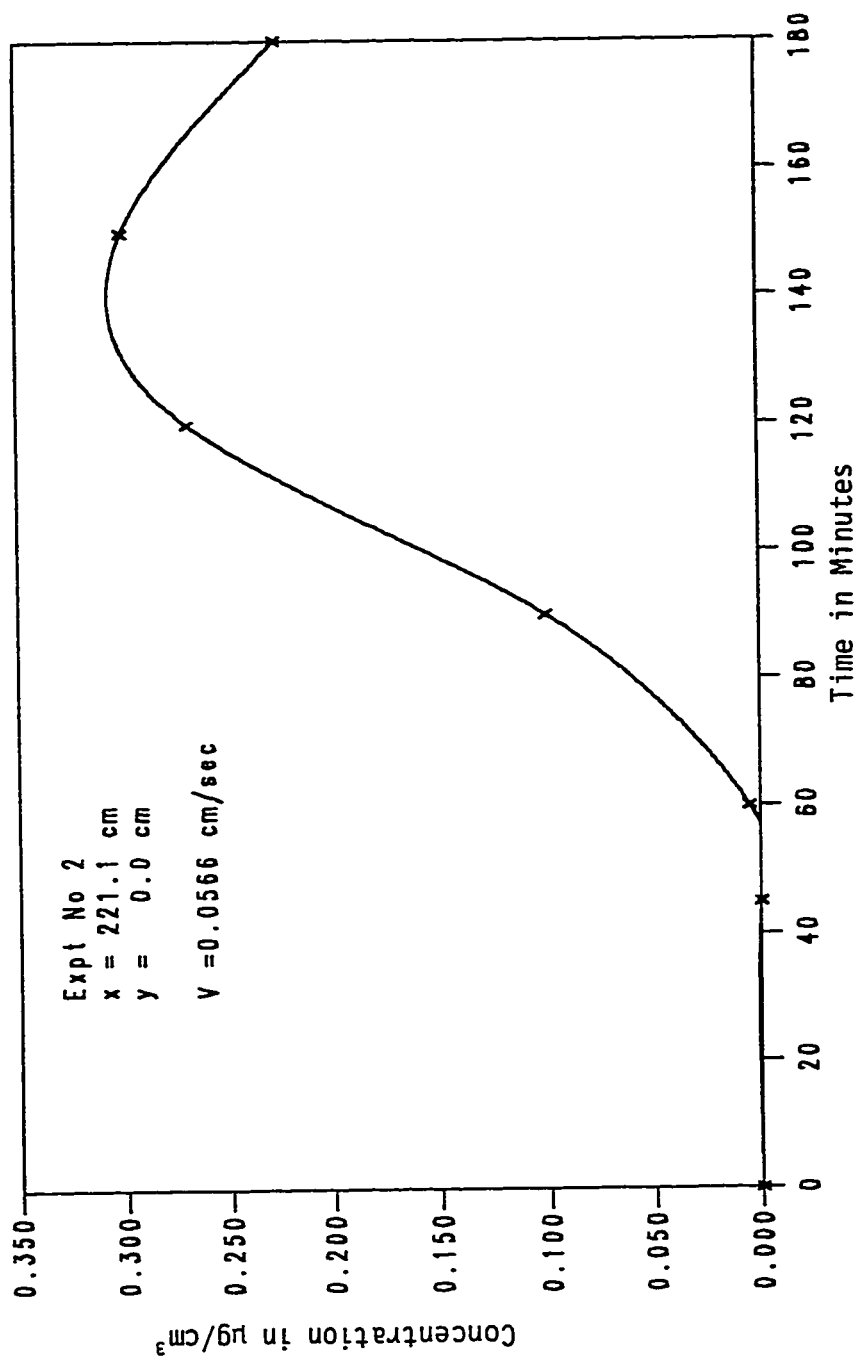


Fig. 5.17. Concentration Variation With Respect to Time.

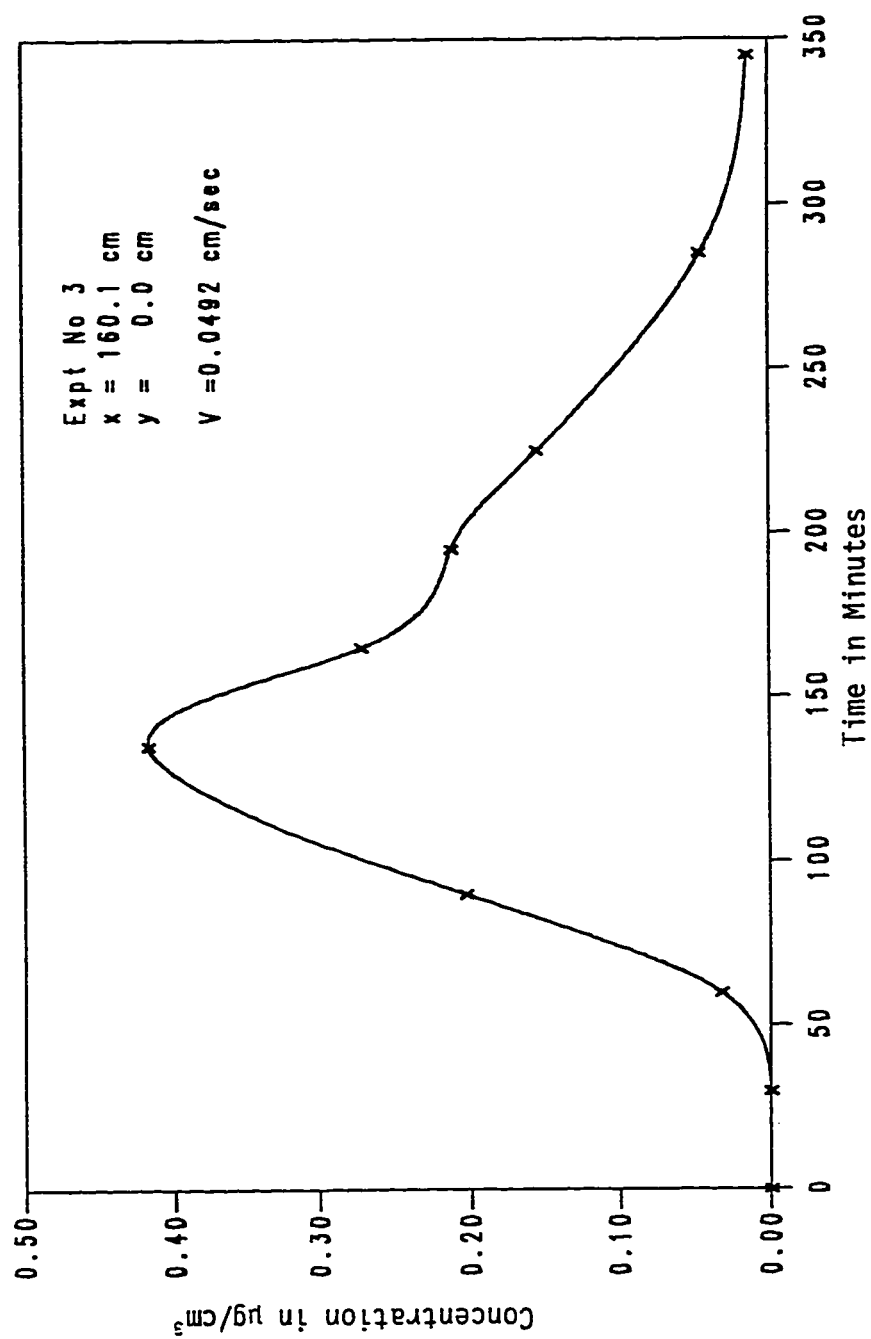


Fig. 5.18. Concentration Variation With Respect to Time.

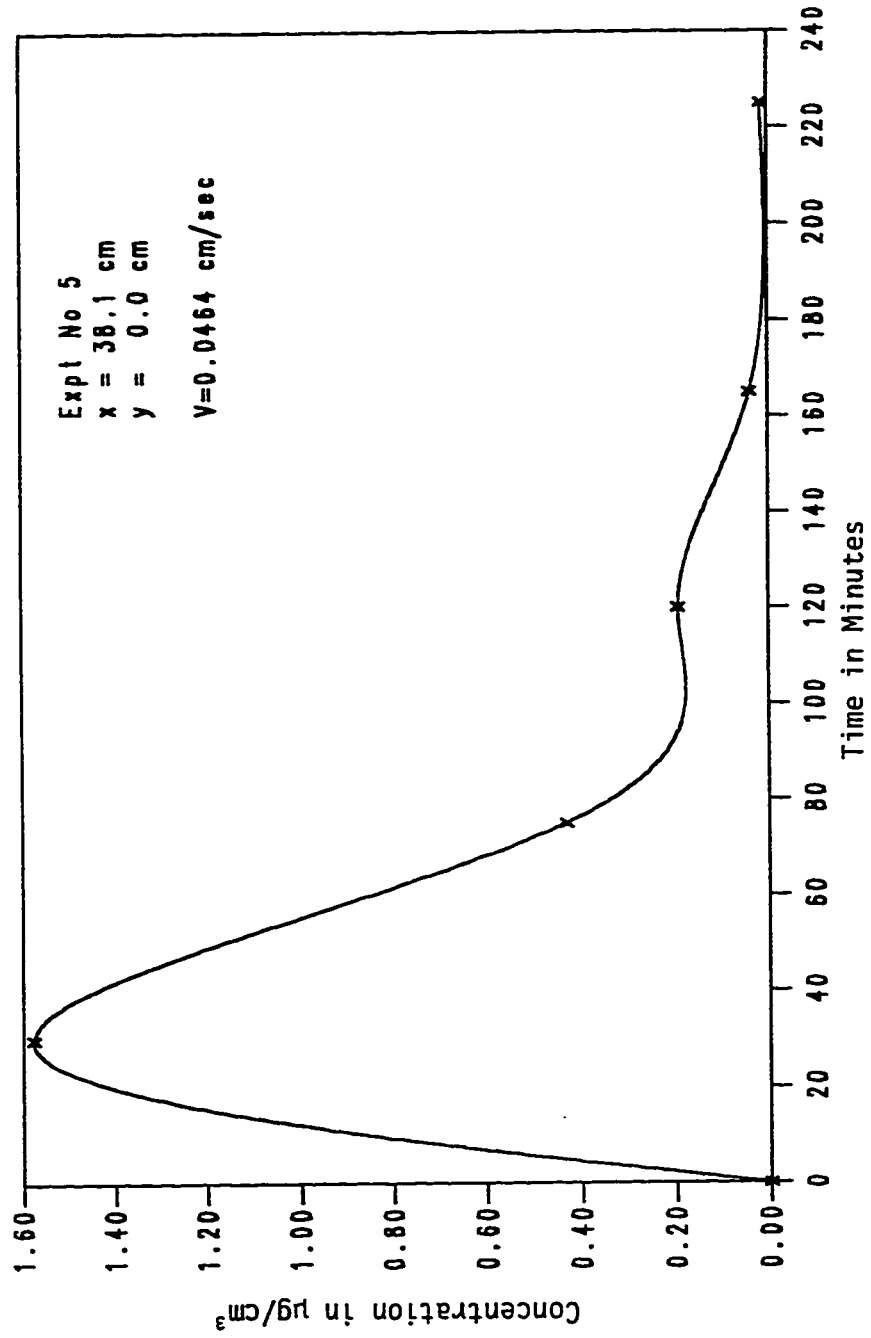


Fig. 5.19. Concentration Variation With Respect to Time.

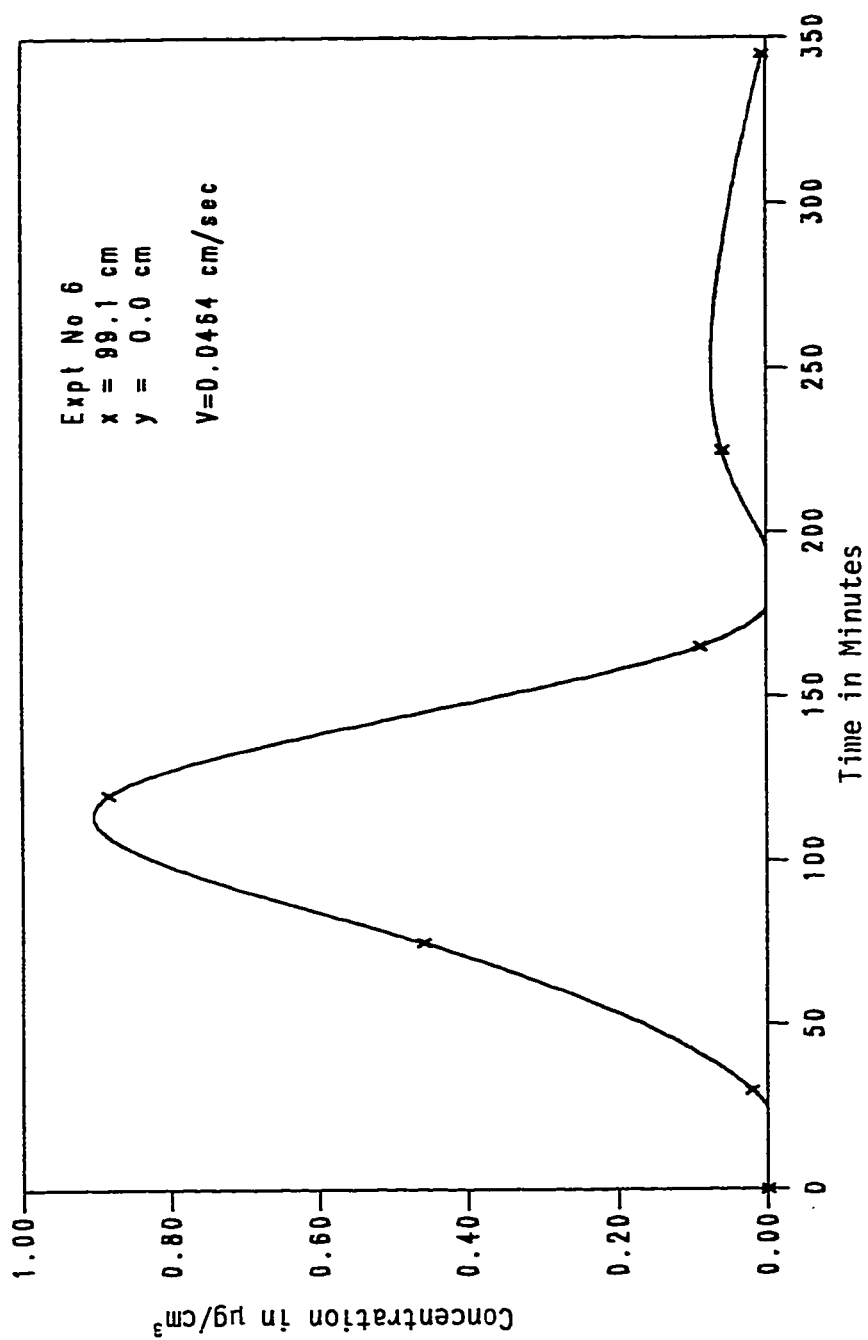


Fig. 5.20. Concentration Variation With Respect to Time.

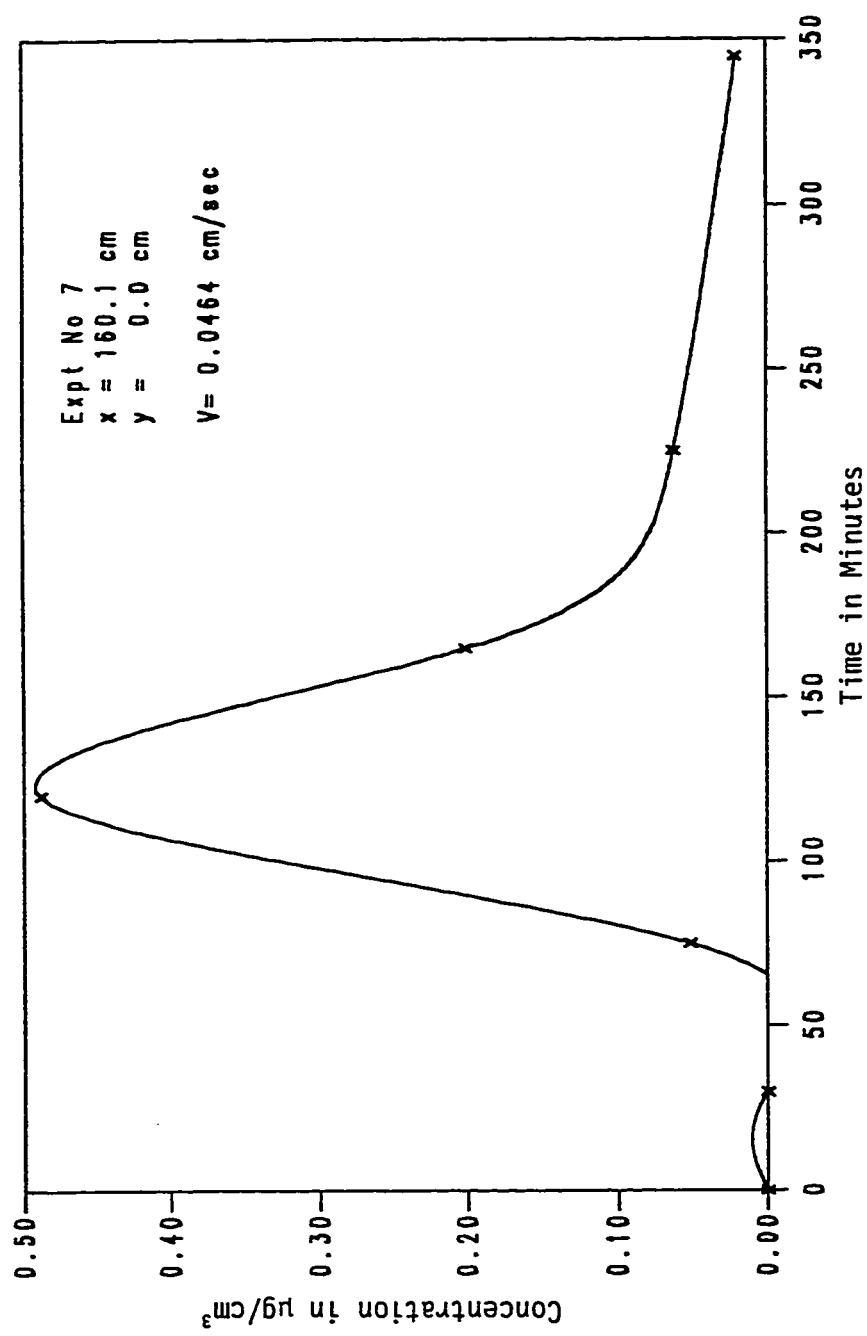


Fig. 5.21. Concentration Variation With Respect to Time.

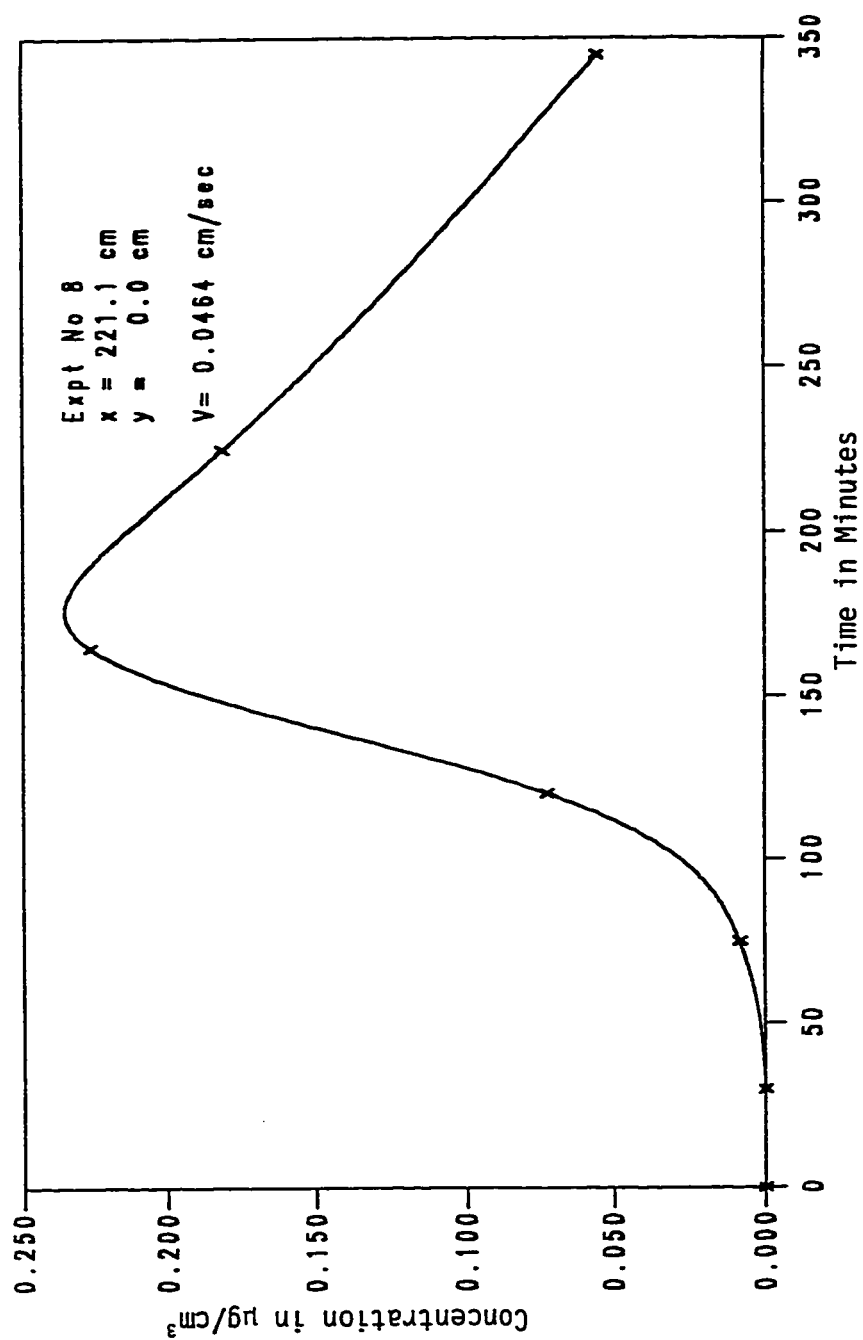


Fig. 5.22. Concentration Variation With Respect to Time.



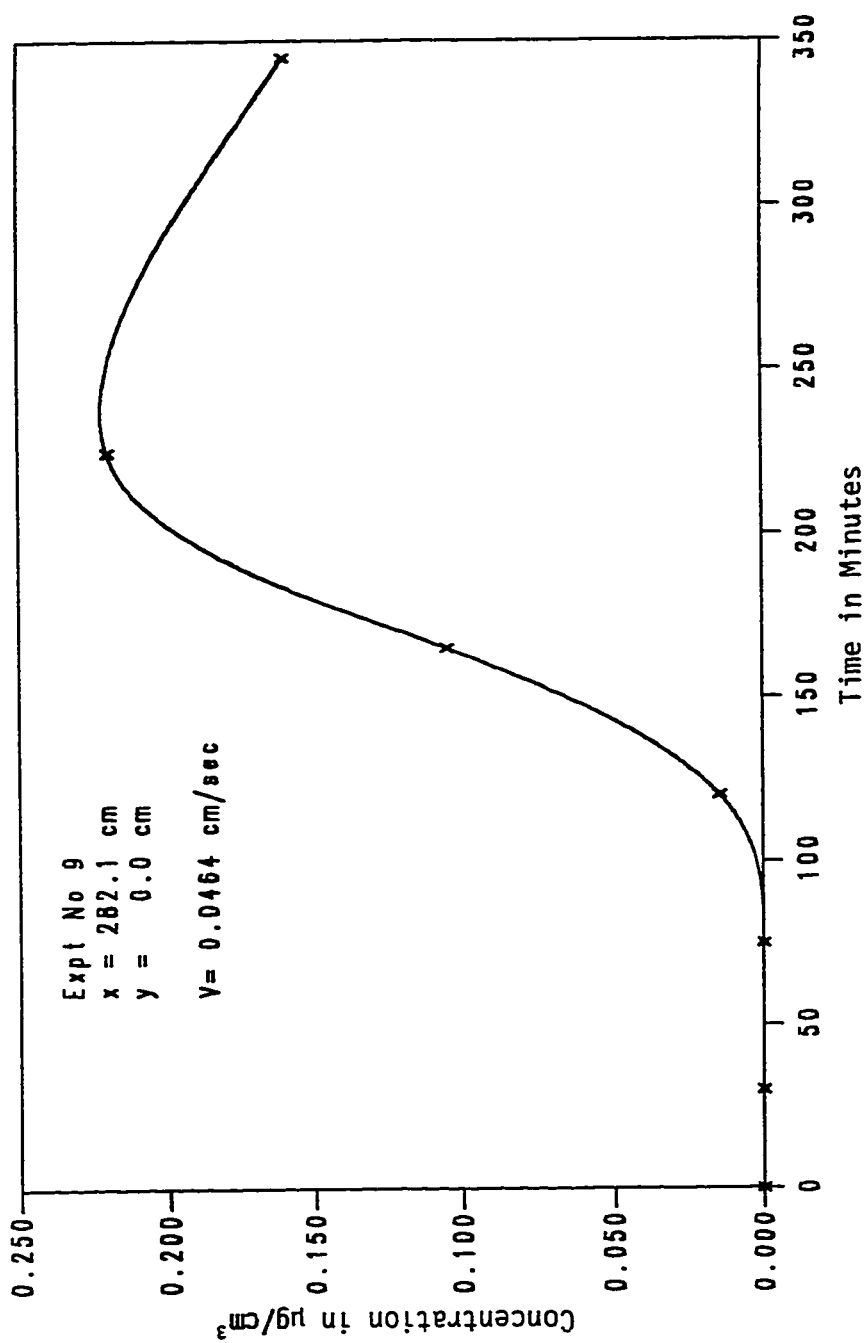


Fig. 5.23. Concentration Variation With Respect to Time.

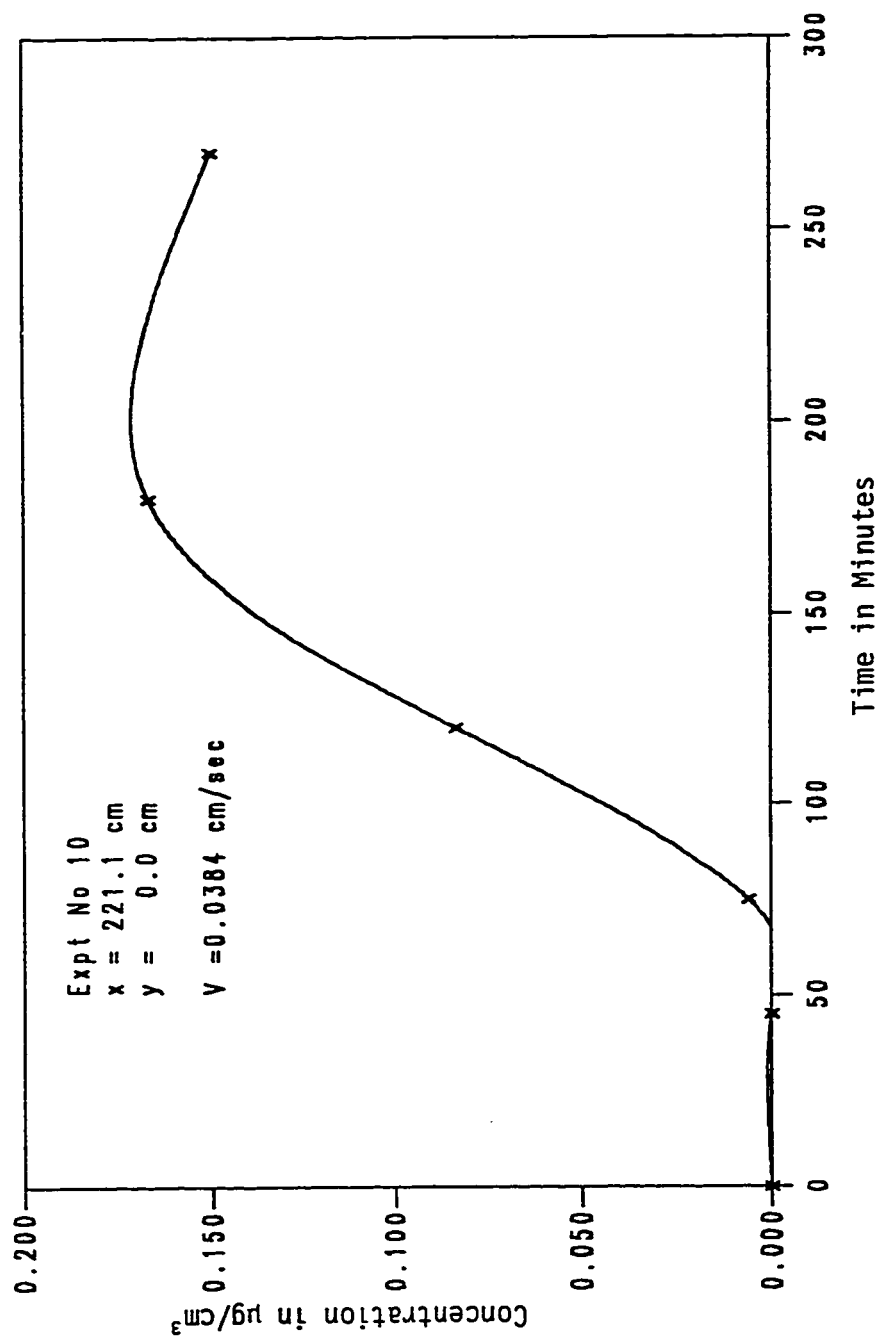


Fig. 5.24. Concentration Variation With Respect to Time.

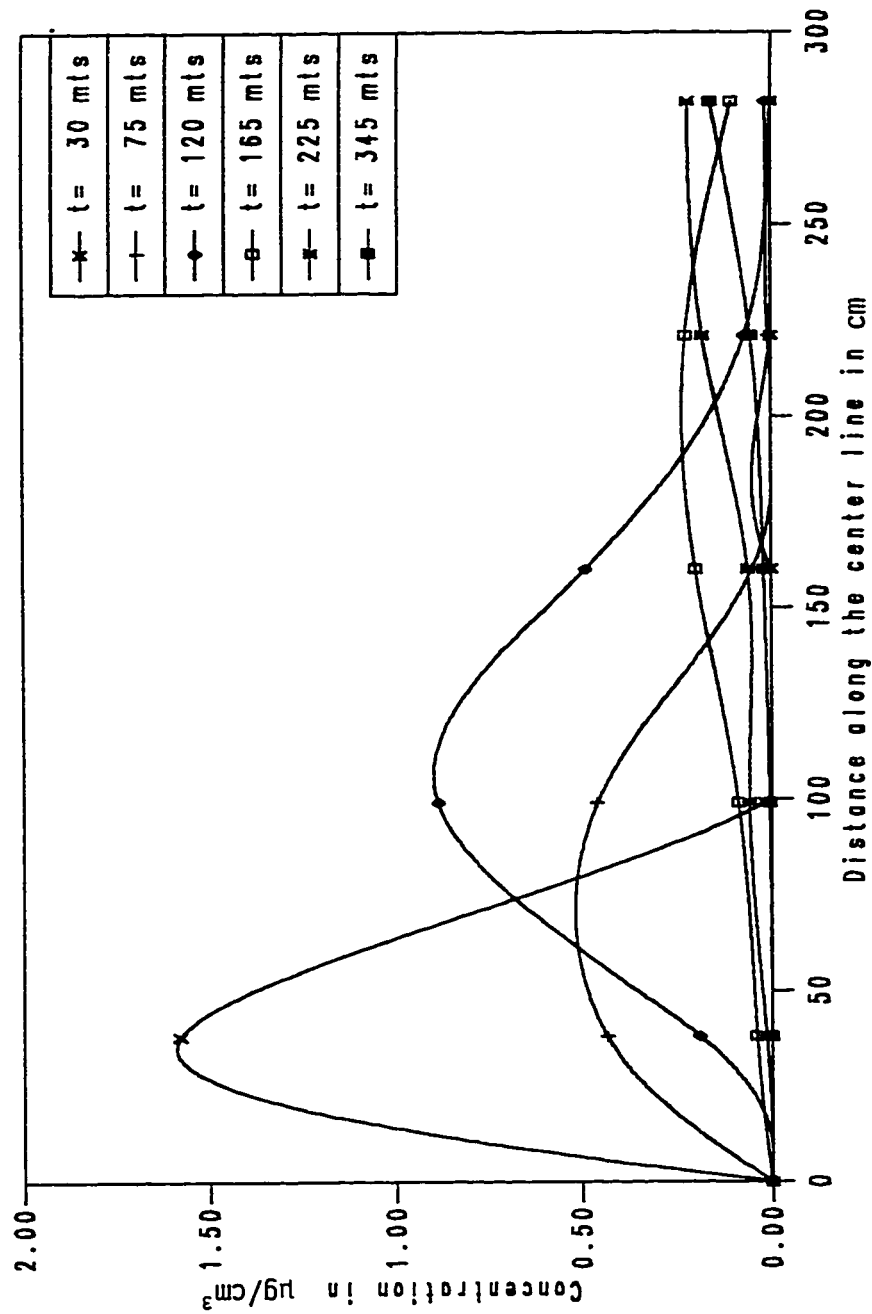


Fig. 5.25. Concentration Variation Along the Direction of Flow at Various Time Intervals.

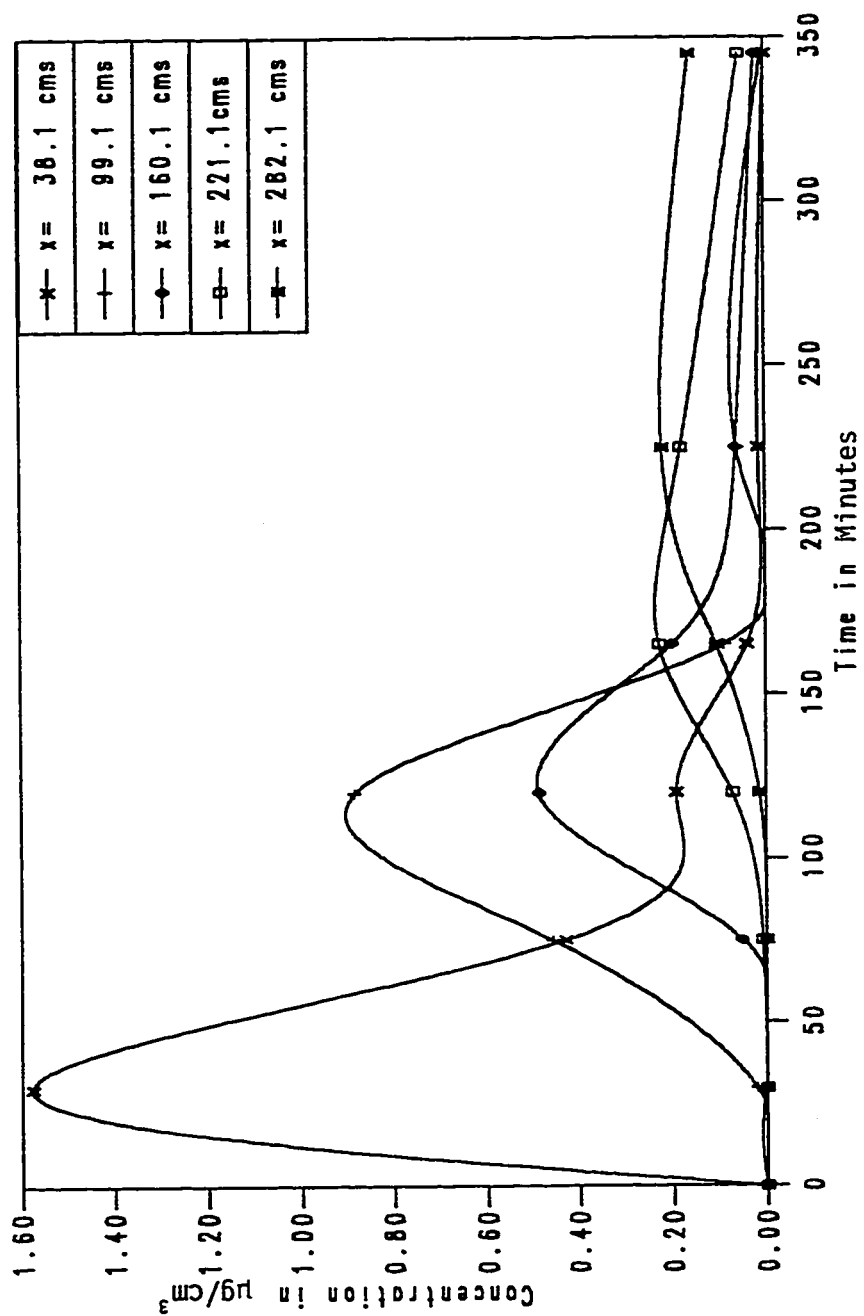


Fig. 5.26. Concentration Variation with Respect to Time Along the Direction of Flow.

concentration increased from  $0.0 \mu\text{g}/\text{cm}^3$  to  $0.488 \mu\text{g}/\text{cm}^3$  during the first 120 min, and then gradually dropped. In a similar manner it was observed that the magnitude of the peak concentration decreased with time and a broadening of the time base occurred. Also, Figure 5.25 shows the development of the plume with respect to time and space. The effect of dispersion can be observed from Figure 5.26, by the flattening of the breakthrough curve before and after attaining the maximum concentrations.

From the experimental results it appears that there is no significant change in the longitudinal dispersion coefficient when the mass of the pollutant injected was varied. A plot of the mass of pollutant injected versus the calculated longitudinal dispersion coefficient is shown in Figure 5.27.

#### 5.4 Determination of the Transverse Dispersion Coefficient

The transverse dispersion coefficient was obtained using the intercept of the straight line obtained resulting from a plot of

$$\frac{\left(x - \frac{\bar{V}_x t}{R}\right)^2}{\frac{4t}{R}} \text{ versus } \ln Ct.$$

The intercept in Eq. (5.5) is given by

$$K_1 = \ln \frac{M}{4\pi n \sqrt{D_x D_y}} \quad (5.8)$$

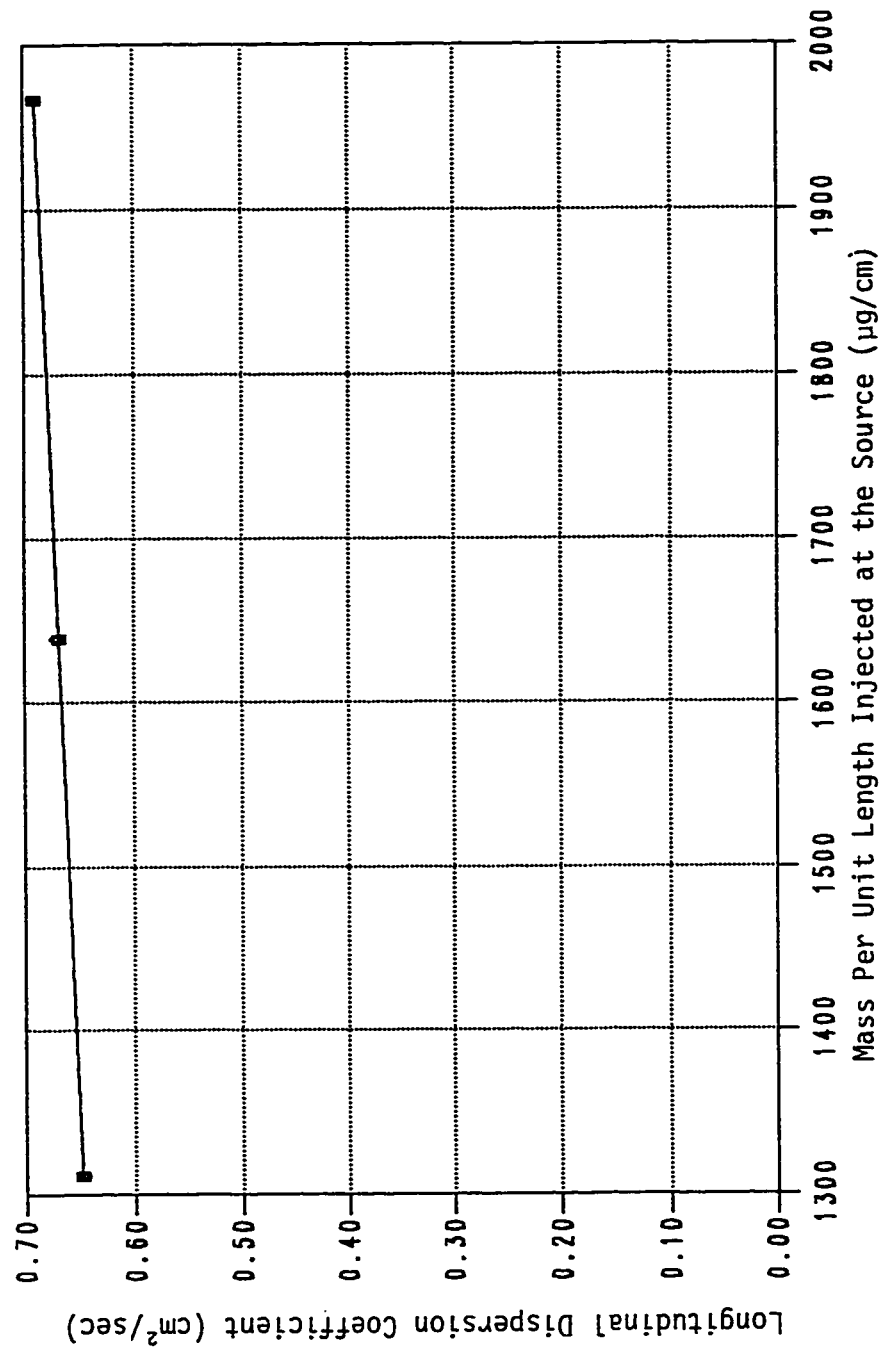


Fig. 5.27. A Plot of the Mass Per Unit Length Injected at the Source versus the Longitudinal Dispersion Coefficient.

A sample calculation of the transverse dispersion coefficient is provided below.

For Experiment # 1

From Figure 5.5

The intercept of the straight line = 8.017

The concentration of the chloroform solution injected

$$= 21700 \text{ ppb } (\mu\text{g/l})$$

$$= 21.7 (\mu\text{g/cm}^3)$$

Mass of chloroform solution injected per unit length

$$= \frac{(21.7)(100)}{14.7} = 147.6 \text{ } \mu\text{g/cm}$$

Longitudinal dispersion coefficient  $D_x = 0.635 \text{ cm}^2/\text{sec}$

$$8.017 = \ln \frac{147.6}{4\pi(0.36)\sqrt{(0.635)D_y}}$$

$$D_y = 1.8 * 10^{-4} \text{ cm}^2/\text{sec}$$

Similarly for the other experiments the transverse dispersion coefficients were calculated, and are shown in Table 5.8. Using a linear regression model the data best fitted a straight line, resulting in a slope which is equivalent to the transverse dispersivity,  $\alpha_y = 0.0039 \text{ cm}$ . From the results of the experiments it can be seen that the transverse dispersivity is much smaller than the longitudinal dispersivity.

Fig. 5.28 shows a plot of concentration at ports located per-

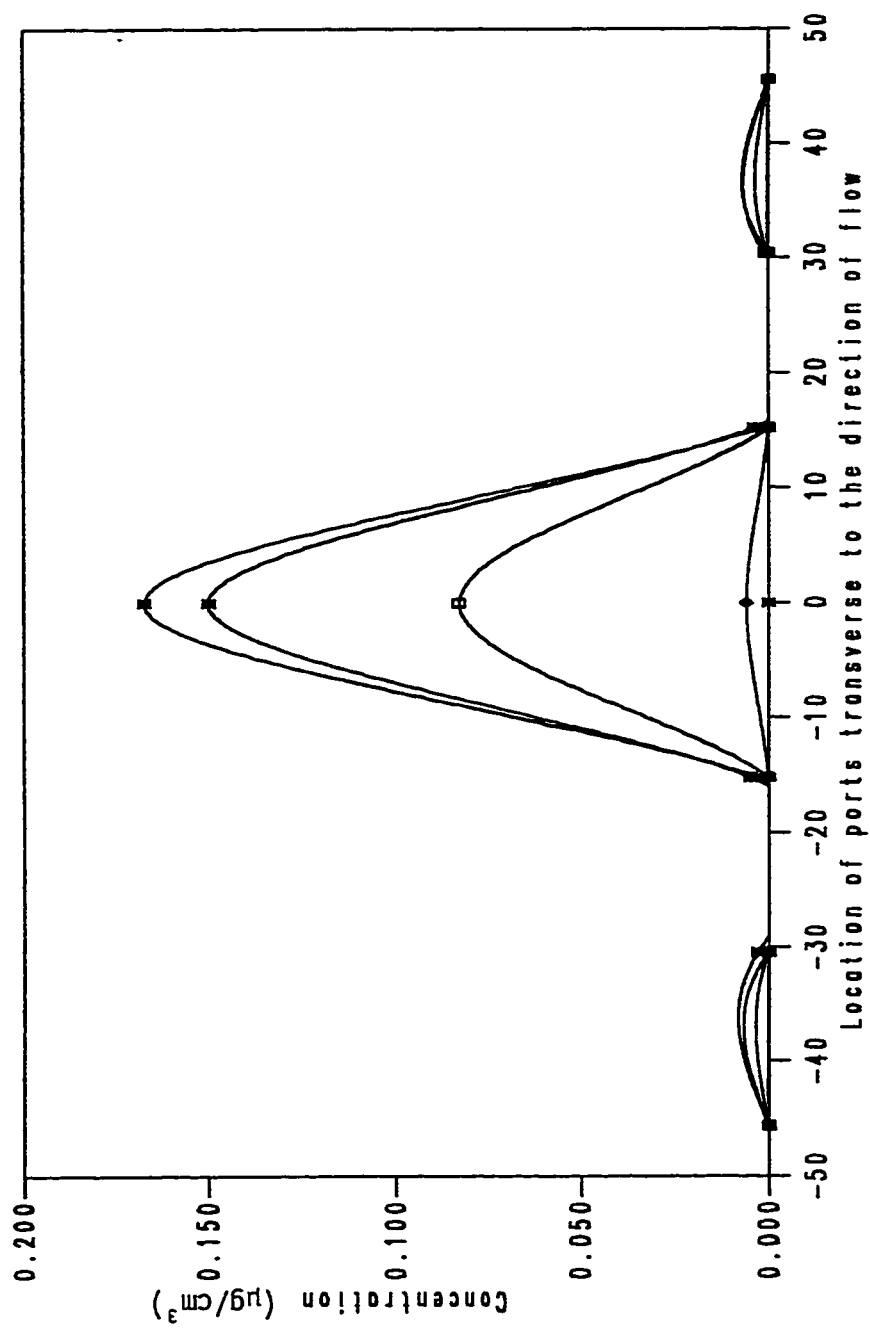


Fig. 5.28. A Plot of Concentration Variation Transverse to the Direction of Flow at Various Time Intervals.



pendicular to the direction of flow at various time intervals, at a distance of 221.1 cm away from the source.

## CHAPTER 6

### 6. CONCLUSIONS AND RECOMMENDATIONS

The following conclusions can be drawn subject to the normal experimental limitations.

1. The longitudinal dispersion coefficient for the chloroform solution injected into the porous medium ranged from 0.60 cm<sup>2</sup>/sec to 0.70 cm<sup>2</sup>/sec.
2. There was no significant change in the longitudinal dispersion coefficient when the average groundwater velocity was varied.
3. The longitudinal dispersivity of the medium used was found to be 0.195 cm. This is within the range of values cited in the literature for laboratory studies (from 0.01 cm to 1 cm).
4. From the limited experimental results there appears to be no significant change in the longitudinal dispersion coefficient when the concentration of the pollutant was varied.
5. The development of the plume was observed very clearly in the experiments conducted. The attenuation effect (decreasing of the peak, and increasing of the time base as the plume moved downstream) too was clearly observed.
6. The transverse dispersion coefficient for the chloroform solution injected into the porous medium ranged from  $0.15 \times 10^{-3}$  cm<sup>2</sup>/sec to  $0.21 \times 10^{-3}$  cm<sup>2</sup>/sec.
7. The transverse dispersivity of the medium used was found to be 0.0039 cm.

8. From the results of the experiments conducted it is evident that the lateral dispersion coefficient is much smaller than the longitudinal dispersion coefficient.
9. The distribution coefficient for chloroform was determined to be 0.20 ml/g. Existing literature cites values of 0.23 to 0.26 ml/g for trichloroethylene.

An appropriate situation for studies of this nature would be to conduct the studies in the field itself. Future laboratory studies may include

- a. To study the behavior of the pollutant for line source injection systems.
- b. To account for biological decay in addition to dispersion, and adsorption.
- c. To provide an automated sampling procedure.

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APPENDIX

**Sieve Analysis**

Sieve No.	Sieve Opening in mm.	Weight of Soil Retained in g	Percent Retained	Cumulative Percent Retained	Percent finer
10	2.000	0	0	0	100.00
16	1.190	26.08	4.28	4.28	95.72
20	0.840	320.79	52.62	56.90	47.38
30	0.590	222.56	36.51	93.41	63.49
40	0.420	34.89	5.72	99.13	94.28
Pan		5.33	0.87	100.00	

### Preparation of a 100 mg/l Chloroform Solution

Density of  $\text{CHCl}_3$  used in the experiments = 1471 mg/ml

1 ml of Chloroform dissolved in 1 l of water will yield a 1471 mg/l solution.

In order to prepare a 1000 mg/l Stock Solution, the volume of Chloroform used =  $\frac{1000}{1471} = 0.68$  ml

In otherwords if 0.68 ml of Chloroform is dissolved in 1 l of water will yield a 1000 mg/l Stock Solution.

i.e. Stock Solution "A" = 1000 mg/l

or 1 mg/1 ml

In order to obtain a 100 mg/l solution of Chloroform, 100 ml of Stock Solution "A" is dissolved in 1 l of water.

i.e. Stock Solution "B" = 100 mg/l = 100 ppm

**Data Sheet # 1****Experiment # 1**

Form of introduction of chloroform solution into the medium - slug input

Volume of chloroform solution injected = 100 ml

Concentration of chloroform solution injected = 21.7 ppm (mg/l)  
 = 21700 ppb ( $\mu\text{g/l}$ )

Samples collected along the center line at  $x = 160.1$  cm and  $y = 0.0$  cm

Volume of water collected at the discharge end =  $1000 \text{ cm}^3$

Time taken to collect  $1000 \text{ cm}^3$  of water = 30.0 secs

Water level in piezometer No. 1 = 131.76 cm

Water level in piezometer No. 2 = 128.90 cm

Water level in piezometer No. 3 = 123.51 cm

Time (min)	Sample #	Area Count	Conc. of $\text{CHCl}_3$ in ppb
0	1	840	0
30	2	852	0
60	3	1161	32
90	4	1793	203
120	5	2369	359
150	6	2417	372
190	7	1852	219
210	8	1648	164
250	9	1656	166
270	10	1202	43
300	11	1124	22

## Data Sheet # 2

## Experiment # 1

$$Q = 33.33 \text{ cm}^3/\text{sec}$$

$$V = 0.0185 \text{ cm/sec}$$

$$n = 0.36$$

$$\bar{V}_x = 0.0511 \text{ cm/sec}$$

$$K = 0.478 \text{ cm/sec}$$

Sampling at

$$x = 160.1 \text{ cm}$$

$$y = 0.0 \text{ cm}$$

$$M = \frac{(100)(21.7)}{14.7} \text{ } \mu\text{g/cm}$$

$$= 147.6 \text{ } \mu\text{g/cm}$$

$$R = 1 + \frac{(2.64)(0.20)}{0.36} = 2.46$$

t (secs)	C ( $\mu\text{g/cm}^3$ )	$(x - \frac{\bar{V}_x t}{R})$ (cm)	$\frac{\bar{V}_x^2 t^2}{4 t/R}$ ( $\text{cm}^2/\text{sec}$ )	ln Ct
0	0.0	-	-	-
1800	0.0	-	-	-
3600	0.032	85.20	1.2381	4.747
5400	0.203	47.75	0.2593	7.000
7200	0.359	10.30	0.0090	7.857
9000	0.372	-27.16	0.0503	8.116
11400	0.219	-77.09	0.3201	7.823
12600	0.164	-102.06	0.5076	7.634
15000	0.064	-151.99	0.9456	6.867
16200	0.043	-176.96	1.1869	6.546
18000	0.022	-214.41	1.5681	5.981



## Data Sheet # 3

## Experiment # 2

Form of introduction of chloroform solution into the medium - slug input

Volume of chloroform solution injected = 100 ml

Concentration of chloroform solution injected = 21.0 ppm (mg/l)  
= 21000 ppb ( $\mu\text{g/l}$ )

Samples collected along the center line at  $x = 221.1$  cm and  $y = 0.0$  cm

Volume of water collected at the discharge end =  $1000 \text{ cm}^3$

Time taken to collect  $1000 \text{ cm}^3$  of water = 27.0 secs

Water level in piezometer No. 1 = 135.41 cm

Water level in piezometer No. 2 = 132.24 cm

Water level in piezometer No. 3 = 126.20 cm

Time (min)	Sample #	Area Count	Conc. of $\text{CHCl}_3$ in ppb
0	1	830	0
45	2	861	0
60	3	1061	5
90	4	1416	101
120	5	2036	269
150	6	2151	300
180	7	1877	226
240	8	903	0
300	9	887	0
360	10	828	0
420	11	1003	0

## Data Sheet # 4

## Experiment # 2

$$Q = 37.04 \text{ cm}^3/\text{sec}$$

$$V = 0.0205 \text{ cm/sec}$$

$$n = 0.36$$

$$\bar{V}_x = 0.0566 \text{ cm/sec}$$

$$K = 0.475 \text{ cm/sec}$$

Sampling at

$$x = 221.1 \text{ cm}$$

$$y = 0.0 \text{ cm}$$

$$M = \frac{(100)(21.0)}{14.7} \text{ } \mu\text{g/cm}$$

$$= 142.8 \text{ } \mu\text{g/cm}$$

$$R = 1 + \frac{(2.64)(0.20)}{0.36} = 2.46$$

t (secs)	C ( $\mu\text{g}/\text{cm}^3$ )	$(x - \frac{\bar{V}_x t}{R})$ (cm)	$\frac{(\bar{V}_x t)^2}{4 t/R}$ ( $\text{cm}^2/\text{sec}$ )	ln Ct
0	0.0	-	-	-
2700	0.0	-	-	-
3600	0.005	138.14	3.2547	2.890
5400	0.101	96.65	1.0621	6.300
7200	0.269	55.17	0.2596	7.569
9000	0.300	13.69	0.0128	7.900
10800	0.226	-27.79	0.0439	7.800
14400	0.0	-	-	-
18000	0.0	-	-	-
21600	0.0	-	-	-
25200	0.0	-	-	-

## Data Sheet # 5

## Experiment # 3

Form of introduction of chloroform solution into the medium - slug  
input

Volume of chloroform solution injected = 100 ml

Concentration of chloroform solution injected = 20.0 ppm (mg/l)  
= 20000 ppb ( $\mu\text{g/l}$ )

Samples collected along the center line at  $x = 160.1$  cm and  $y = 0.0$   
cm

Volume of water collected at the discharge end =  $1000 \text{ cm}^3$

Time taken to collect  $1000 \text{ cm}^3$  of water = 31.2 secs

Water level in piezometer No. 1 = 130.17 cm

Water level in piezometer No. 2 = 127.79 cm

Water level in piezometer No. 3 = 122.87 cm

Time (min)	Sample #	Area Count	Conc. of $\text{CHCl}_3$ in ppb
0	1	837	0
30	2	1005	0
60	3	1161	32
90	4	1793	203
135	5	2583	417
165	6	2044	271
195	7	1826	212
225	8	1615	155
285	9	1209	45
345	10	1095	14

## Data Sheet # 6

## Experiment # 3

$$Q = 32.05 \text{ cm}^3/\text{sec}$$

$$V = 0.0178 \text{ cm/sec}$$

$$n = 0.36$$

$$\bar{V}_x = 0.0492 \text{ cm/sec}$$

$$K = 0.520 \text{ cm/sec}$$

## Sampling at

$$x = 160.1 \text{ cm}$$

$$y = 0.0 \text{ cm}$$

$$M = \frac{(100)(20.0)}{14.7} \text{ } \mu\text{g/cm}$$

$$= 136.0 \text{ } \mu\text{g/cm}$$

$$R = 1 + \frac{(2.64)(0.20)}{0.36} = 2.46$$

t (secs)	C ( $\mu\text{g/cm}^3$ )	$(x - \frac{\bar{V}_x t}{R})$ (cm)	$\frac{(\bar{V}_x t)^2}{4 t/R}$ ( $\text{cm}^2/\text{sec}$ )	ln Ct
0	0.0	-	-	-
1800	0.0	-	-	-
3600	0.032	87.98	1.3202	4.747
5400	0.203	51.92	0.3065	7.000
8100	0.417	-2.16	0.0004	8.125
9900	0.271	-38.22	0.0906	7.895
11700	0.212	-74.28	0.2895	7.816
13500	0.155	-110.34	0.5537	7.646
17100	0.045	-182.46	1.1954	6.646
20700	0.014	-254.57	1.9223	5.669

## Data Sheet # 7

## Experiment # 4

Form of introduction of chloroform solution into the medium - slug input

Volume of chloroform solution injected = 100 ml

Concentration of chloroform solution injected = 23.2 ppm (mg/l)  
 = 23200 ppb ( $\mu\text{g/l}$ )

Samples collected along the center line at  $x = 251.6$  cm and  $y = 0.0$  cm

Volume of water collected at the discharge end =  $1000 \text{ cm}^3$

Time taken to collect  $1000 \text{ cm}^3$  of water = 45.9 secs

Water level in piezometer No. 1 = 136.36 cm

Water level in piezometer No. 2 = 135.09 cm

Water level in piezometer No. 3 = 132.08 cm

Time (min)	Sample #	Area Count	Conc. of $\text{CHCl}_3$ in ppb
0	1	889	0
45	2	1004	0
75	3	1021	0
105	4	1076	9
135	5	1080	10
165	6	1150	29
195	7	1246	55
225	8	1257	58
285	9	1810	208
345	10	2176	307

## Data Sheet # 8

## Experiment # 4

$$Q = 21.79 \text{ cm}^3/\text{sec}$$

$$V = 0.0121 \text{ cm/sec}$$

$$n = 0.36$$

$$\bar{V}_x = 0.0334 \text{ cm/sec}$$

$$K = 0.602 \text{ cm/sec}$$

Sampling at

$$x = 251.6 \text{ cm}$$

$$y = 0.0 \text{ cm}$$

$$M = \frac{(100)(23.2)}{14.7} \text{ } \mu\text{g/cm}$$

$$= 157.8 \text{ } \mu\text{g/cm}$$

$$R = 1 + \frac{(2.64)(0.20)}{0.36} = 2.46$$

t (secs)	C ( $\mu\text{g}/\text{cm}^3$ )	$(x - \frac{\bar{V}_x t}{R})$ (cm)	$\frac{\bar{V}_x^2 t^2}{4 t/R}$ ( $\text{cm}^2/\text{sec}$ )	ln Ct
0	0.0	-	-	-
2700	0.0	-	-	-
4500	0.0	-	-	-
6300	0.009	165.92	2.6830	4.038
8100	0.010	141.45	1.5167	4.400
9900	0.029	116.97	0.8485	5.660
11700	0.055	92.49	0.4489	6.467
13500	0.058	68.01	0.2104	6.663
17100	0.208	19.05	0.0130	8.177
20700	0.307	-29.91	0.0265	8.757

## Data Sheet # 9

## Experiment # 5

Form of introduction of chloroform solution into the medium - slug input

Volume of chloroform solution injected = 100 ml

Concentration of chloroform solution injected = 23.3 ppm (mg/l)  
 = 23300 ppb ( $\mu\text{g/l}$ )

Samples collected along the center line at  $x = 38.1$  cm and  $y = 0.0$  cm

Volume of water collected at the discharge end =  $1000 \text{ cm}^3$

Time taken to collect  $1000 \text{ cm}^3$  of water = 33.0 secs

Water level in piezometer No. 1 = 128.75 cm

Water level in piezometer No. 2 = 126.52 cm

Water level in piezometer No. 3 = 122.08 cm

Time (min)	Sample #	Area Count	Conc. of $\text{CHCl}_3$ in ppb
0	1	936	0
30	2	6867	1577
75	3	2631	430
120	4	1752	192
165	5	1194	41
225	6	1098	15

## Data Sheet # 10

## Experiment # 5

$$Q = 30.30 \text{ cm}^3/\text{sec}$$

$$V = 0.0168 \text{ cm/sec}$$

$$n = 0.36$$

$$\bar{V}_x = 0.0464 \text{ cm/sec}$$

$$K = 0.537 \text{ cm/sec}$$

Sampling at

$$x = 38.1 \text{ cm}$$

$$y = 0.0 \text{ cm}$$

$$M = \frac{(100)(23.3)}{14.7} \text{ } \mu\text{g/cm}$$

$$= 158.8 \text{ } \mu\text{g/cm}$$

$$R = 1 + \frac{(2.64)(0.20)}{0.36} = 2.46$$

t (secs)	C ( $\mu\text{g}/\text{cm}^3$ )	$(x - \frac{\bar{V}_x t}{R})$ (cm)	$\frac{(\bar{V}_x t)^2}{4 t/R}$ ( $\text{cm}^2/\text{sec}$ )	ln Ct
0	0.0	-	-	-
1800	1.577	-9.91	0.0335	7.951
4500	0.430	-60.92	0.5064	7.568
7200	0.192	-111.93	1.0684	7.232
9900	0.041	-148.94	1.3758	6.006
13500	0.015	-216.95	2.1407	5.311



## Data Sheet # 11

## Experiment # 6

Form of introduction of chloroform solution into the medium - slug input

Volume of chloroform solution injected = 100 ml

Concentration of chloroform solution injected = 24.2 ppm (mg/l)  
 = 24200 ppb ( $\mu\text{g/l}$ )

Samples collected along the center line at  $x = 99.1$  cm and  $y = 0.0$  cm

Volume of water collected at the discharge end =  $1000 \text{ cm}^3$

Time taken to collect  $1000 \text{ cm}^3$  of water = 33.0 secs

Water level in piezometer No. 1 = 128.75 cm

Water level in piezometer No. 2 = 126.52 cm

Water level in piezometer No. 3 = 122.08 cm

Time (min)	Sample #	Area Count	Conc. of $\text{CHCl}_3$ in ppb
0	1	937	0
30	2	1120	21
75	3	2734	458
120	4	4307	884
165	5	1372	89
225	6	1264	60
345	7	1065	6

## Data Sheet # 12

## Experiment # 6

$$Q = 30.30 \text{ cm}^3/\text{sec}$$

$$V = 0.0168 \text{ cm/sec}$$

$$n = 0.36$$

$$\bar{V}_x = 0.0464 \text{ cm/sec}$$

$$K = 0.537 \text{ cm/sec}$$

Sampling at

$$x = 99.1 \text{ cm}$$

$$y = 0.0 \text{ cm}$$

$$M = \frac{(100)(24.2)}{14.7} \text{ } \mu\text{g/cm}$$

$$= 164.8 \text{ } \mu\text{g/cm}$$

$$R = 1 + \frac{(2.64)(0.20)}{0.36} = 2.46$$

t (secs)	C ( $\mu\text{g/cm}^3$ )	$(x - \frac{\bar{V}_x t}{R})$ (cm)	$\frac{(\bar{V}_x t^2 - \frac{x^2}{R})}{4 t/R}$ ( $\text{cm}^2/\text{sec}$ )	ln Ct
0	0.0	-	-	-
1800	0.021	65.09	1.4452	3.632
4500	0.458	14.08	0.0270	7.631
7200	0.884	-36.93	0.1163	8.758
9900	0.089	-87.94	0.4796	6.781
13500	0.060	-155.95	1.1061	6.694
20700	0.006	-291.97	2.5286	4.822

## Data Sheet # 13

## Experiment # 7

Form of introduction of chloroform solution into the medium - slug  
input

Volume of chloroform solution injected = 100 ml

Concentration of chloroform solution injected = 24.2 ppm (mg/l)  
= 24200 ppb ( $\mu\text{g/l}$ )

Samples collected along the center line at  $x = 160.1$  cm and  $y = 0.0$   
cm

Volume of water collected at the discharge end =  $1000 \text{ cm}^3$

Time taken to collect  $1000 \text{ cm}^3$  of water = 33.0 secs

Water level in piezometer No. 1 = 128.75 cm

Water level in piezometer No. 2 = 126.52 cm

Water level in piezometer No. 3 = 122.08 cm

Time (min)	Sample #	Area Count	Conc. of $\text{CHCl}_3$ in ppb
0	1	876	0
30	2	1003	0
75	3	1235	52
120	4	2845	488
165	5	1785	201
225	6	1276	63
345	7	1120	21

## Data Sheet # 14

## Experiment # 7

$$Q = 30.30 \text{ cm}^3/\text{sec}$$

$$V = 0.0168 \text{ cm/sec}$$

$$n = 0.36$$

$$\bar{V}_x = 0.0464 \text{ cm/sec}$$

$$K = 0.537 \text{ cm/sec}$$

Sampling at

$$x = 160.1 \text{ cm}$$

$$y = 0.0 \text{ cm}$$

$$M = \frac{(100)(24.2)}{14.7} \text{ } \mu\text{g/cm}$$

$$= 164.8 \text{ } \mu\text{g/cm}$$

$$R = 1 + \frac{(2.64)(0.20)}{0.36} = 2.46$$

t (secs)	C ( $\mu\text{g/cm}^3$ )	$(x - \frac{\bar{V}_x t}{R})$ (cm)	$\frac{\bar{V}_x t^2}{4 t/R}$ ( $\text{cm}^2/\text{sec}$ )	ln Ct
0	0.0	-	-	-
1800	0.0	-	-	-
4500	0.052	75.08	0.7691	5.455
7200	0.488	24.07	0.0494	8.164
9900	0.201	-26.94	0.0450	7.596
13500	0.063	-94.95	0.4100	6.746
20700	0.021	-230.97	1.5824	6.075

## Data Sheet # 15

## Experiment # 8

Form of introduction of chloroform solution into the medium - slug input

Volume of chloroform solution injected = 100 ml

Concentration of chloroform solution injected = 24.2 ppm (mg/l)

= 24200 ppb ( $\mu\text{g/l}$ )

Samples collected along the center line at  $x = 221.1$  cm and  $y = 0.0$  cm

Volume of water collected at the discharge end =  $1000 \text{ cm}^3$

Time taken to collect  $1000 \text{ cm}^3$  of water = 33.0 secs

Water level in piezometer No. 1 = 128.75 cm

Water level in piezometer No. 2 = 126.52 cm

Water level in piezometer No. 3 = 122.08 cm

Time (min)	Sample #	Area Count	Conc. of $\text{CHCl}_3$ in ppb
0	1	967	0
30	2	894	0
75	3	1072	8
120	4	1309	72
165	5	1881	227
225	6	1711	181
345	7	1246	55

## Data Sheet # 16

## Experiment # 8

$$Q = 30.30 \text{ cm}^3/\text{sec}$$

$$V = 0.0168 \text{ cm/sec}$$

$$n = 0.36$$

$$\bar{V}_x = 0.0464 \text{ cm/sec}$$

$$K = 0.537 \text{ cm/sec}$$

## Sampling at

$$x = 221.1 \text{ cm}$$

$$y = 0.0 \text{ cm}$$

$$M = \frac{(100)(24.2)}{14.7} \text{ } \mu\text{g/cm}$$

$$= 164.8 \text{ } \mu\text{g/cm}$$

$$R = 1 + \frac{(2.64)(0.20)}{0.36} = 2.46$$

t (secs)	C ( $\mu\text{g/cm}^3$ )	$(x - \frac{\bar{V}_x t}{R})$ (cm)	$\frac{(\bar{V}_x t)^2}{4 t/R}$ ( $\text{cm}^2/\text{sec}$ )	ln Ct
0	0.0	-	-	-
1800	0.0	-	-	-
4500	0.008	136.08	2.5266	3.584
7200	0.072	85.07	0.6171	6.251
9900	0.227	34.06	0.0719	7.717
13500	0.181	-33.95	0.0524	7.801
20700	0.055	-169.97	0.8569	7.037

## Data Sheet # 17

## Experiment # 9

Form of introduction of chloroform solution into the medium - slug input

Volume of chloroform solution injected = 100 ml

Concentration of chloroform solution injected = 24.2 ppm (mg/l)  
 = 24200 ppb ( $\mu\text{g/l}$ )

Samples collected along the center line at  $x = 282.1$  cm and  $y = 0.0$  cm

Volume of water collected at the discharge end =  $1000 \text{ cm}^3$

Time taken to collect  $1000 \text{ cm}^3$  of water = 33.0 secs

Water level in piezometer No. 1 = 128.75 cm

Water level in piezometer No. 2 = 126.52 cm

Water level in piezometer No. 3 = 122.08 cm

Time (min)	Sample #	Area Count	Conc. of $\text{CHCl}_3$ in ppb
0	1	846	0
30	2	878	0
75	3	961	0
120	4	1098	15
165	5	1431	105
225	6	1855	220
345	7	1634	160

## Data Sheet # 18

## Experiment # 9

$$Q = 30.30 \text{ cm}^3/\text{sec}$$

$$V = 0.0168 \text{ cm/sec}$$

$$n = 0.36$$

$$\bar{V}_x = 0.0464 \text{ cm/sec}$$

$$K = 0.537 \text{ cm/sec}$$

## Sampling at

$$x = 282.1 \text{ cm}$$

$$y = 0.0 \text{ cm}$$

$$M = \frac{(100)(24.2)}{14.7} \text{ } \mu\text{g/cm}$$

$$= 164.8 \text{ } \mu\text{g/cm}$$

$$R = 1 + \frac{(2.64)(0.20)}{0.36} = 2.46$$

t (secs)	C ( $\mu\text{g/cm}^3$ )	$(x - \frac{\bar{V}_x t}{R})$ (cm)	$\frac{(\bar{V}_x t)^2}{4 t/R}$ ( $\text{cm}^2/\text{sec}$ )	ln Ct
0	0.0	-	-	-
1800	0.0	-	-	-
4500	0.0	-	-	-
7200	0.015	146.07	1.8195	4.682
9900	0.105	95.06	0.5604	6.946
13500	0.220	27.05	0.0333	7.996
20700	0.160	-108.97	0.3522	8.105



## Data Sheet # 19

## Experiment # 10

Form of introduction of chloroform solution into the medium - slug input

Volume of chloroform solution injected = 100 ml

Concentration of chloroform solution injected = 16.7 ppm (mg/l)

= 16700 ppb ( $\mu\text{g/l}$ )

Samples collected along the center line at  $x = 221.1$  cm and  $y = 0.0$  cm

Volume of water collected at the discharge end =  $1000 \text{ cm}^3$

Time taken to collect  $1000 \text{ cm}^3$  of water = 39.9 secs

Water level in piezometer No. 1 = 133.03 cm

Water level in piezometer No. 2 = 131.76 cm

Water level in piezometer No. 3 = 128.43 cm

Time (min)	Sample #	Area Count	Conc. of $\text{CHCl}_3$ in ppb
0	1	871	0
45	2	939	0
75	3	1065	6
120	4	1349	83
180	5	1660	167
270	6	1597	150

## Data Sheet # 20

## Experiment # 10

$$Q = 25.06 \text{ cm}^3/\text{sec}$$

$$V = 0.0139 \text{ cm/sec}$$

$$n = 0.36$$

$$\bar{V}_x = 0.0384 \text{ cm/sec}$$

$$K = 0.644 \text{ cm/sec}$$

## Sampling at

$$x = 222.1 \text{ cm}$$

$$y = 0.0 \text{ cm}$$

$$M = \frac{(100)(16.7)}{14.7} \mu\text{g/cm}$$

$$= 113.4 \mu\text{g/cm}$$

$$R = 1 + \frac{(2.64)(0.20)}{0.36} = 2.46$$

$t$ (secs)	$C$ ( $\mu\text{g}/\text{cm}^3$ )	$(x - \frac{\bar{V}_x t}{R})$ (cm)	$\frac{(\bar{V}_x t)^2}{4 t/R}$ ( $\text{cm}^2/\text{sec}$ )	$\ln Ct$
0	0.0	-	-	-
2700	0.0	-	-	-
4500	0.006	150.74	3.1004	3.295
7200	0.083	108.53	1.0045	6.393
10800	0.167	52.24	0.1551	7.497
16200	0.150	-32.19	0.0393	7.796